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(54) **Non-Ideal Barrier coating sequence composition**

(57) The present invention is a non-ideal barrier coating sequence composition comprising oxides and organic polymers. The non-ideal barrier coating sequence composition is useful for providing an effective barrier against gas permeability in containers and for extending shelf-life of containers, especially plastic evacuated blood collection devices.

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EUROPEAN SEARCH REPORT

Application Number
EP 97 10 1065

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.CI.8)
X	WO 95 10117 A (CATALINA COATINGS INC ; SHAW DAVID G (US); DAWSON ERIC (US); CLINE) 13 April 1995 (1995-04-13) * page 4, line 30 - page 9, line 14; claims 1,2,18 *	1-12, 16-27, 31-36, 43-51, 55,57	C23C16/40 A61J1/00 C08J7/04 B65D23/08 B05D7/00
X	DE 44 04 690 A (LEYBOLD AG) 17 August 1995 (1995-08-17)	1-4,6-8, 16-19, 21-23, 31-33, 35,36, 45-47, 55	
A	* column 2, line 45 - column 3, line 9; claims 1,5,8-14 *		
X	EP 0 607 573 A (BECTON DICKINSON CO) 27 July 1994 (1994-07-27) * claims *	1-8,13, 16-23, 28, 31-36, 44-47	TECHNICAL FIELDS SEARCHED (Int.CI.8) C23C
X	PATENT ABSTRACTS OF JAPAN vol. 016, no. 103 (M-1221), 13 March 1992 (1992-03-13) & JP 03 278946 A (OIKE IND CO LTD), 10 December 1991 (1991-12-10) * abstract *	1-8, 16-23	
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 23 March 2001	Examiner Patterson, A
<p>CATEGORY OF CITED DOCUMENTS</p> <p>X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document</p> <p>T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document</p>			

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between 150 and 1,000 and a vapor pressure in the range of 1×10^{-6} to 1×10^{-1} Torr at standard temperature and pressure. Most preferably, the material is a diacrylate.

The organic material provides a platform for deposition of the inorganic material. Preferably, the thickness of the acrylate material is about 0.1 microns to about 10 microns and most preferably from about 0.5 microns to about 3 microns.

Desirably, the inorganic material is a metal oxide, such as a silicon oxide based composition, such as SiO_x wherein x is from about 1.0 to about 2.5; or an aluminium oxide based composition. Most preferably, the organic material is a highly cross linked acrylate polymer.

The silicon oxide based composition is substantially dense and vapor-impervious and is desirably derived from volatile organosilicon compounds and acrylate. Preferably, the thickness of the silicon oxide based material is about 100 to about 2,000 Angstroms (\AA) and most preferably from about 500 to about 1,000 \AA . A material above 5,000 \AA may crack and therefore be ineffective as a barrier.

An optional organic material may be disposed over the non-ideal barrier coating sequence composition and preferably comprises vinylidene chloride - methyl methacrylate - methacrylate acrylic acid polymer (PVDC), thermosetting epoxy materials, parylene polymers or polyesters.

Preferably, the thickness of the PVDC material is about 2 to about 15 microns and most preferably from about 3 to about 5 microns.

The process for applying the organic material of the sequence is preferably carried out in a vacuum chamber wherein a curable monomer component is metered to a heated vaporizer system where the material is atomized, vaporized and condensed on the surface of the container. Following deposit of the monomer onto the surface of the container, it is cured by suitable means such as electron beam curing. The deposition and curing steps may be repeated until the desired thickness of materials has been achieved.

A method for depositing a silicon oxide based material is as follows: (a) pretreating the organic material on the container with a first plasma material of oxygen; (b) controllably flowing a gas stream including an organosilicon compound into a plasma; and (c) depositing a silicon oxide onto the organic material while maintaining a pressure of less than about 500 mTorr during the depositing.

The organosilicon compound is preferably combined with oxygen and optionally helium or another inert gas such as argon or nitrogen and at least a portion of the plasma is preferably magnetically confined adjacent to the surface of the organic material during the depositing, most preferably by an unbalanced magnetron.

Although the pretreatment step is optional, it is believed that the oxygen plasma pretreatment step provides for improved adherence qualities between the organic material and the organic material.

The PVDC material is optionally applied over the non-ideal barrier coating sequence composition by dipping or spraying and then followed by air drying at about 50°C .

Most preferably, the method for depositing non-ideal a barrier coating sequence composition on a substrate, such as a plastic collection tube comprises the following steps:

- (a) selecting a curable component comprising: i) polyfunctional acrylates, or ii) mixtures of monoacrylates and polyfunctional acrylates;
- (b) flash vaporizing the component into the chamber;
- (c) condensing an organic material of a vaporized component onto the outer surface of the container;
- (d) curing the organic material;
- (e) vaporizing an organosilicon component and admixing the volatilized organosilicon component with an oxidizer component and optionally an inert gas component to form a gas stream exterior to the chamber;
- (f) controllably flowing the gas stream into the chamber;
- (g) establishing a glow discharge plasma in the chamber from the gas stream;
- (h) depositing a silicon oxide material adjacent the organic material;
- (i) repeating steps (a) through (d) above, thereby depositing an acrylate material adjacent the silicon oxide material; and
- (j) repeating steps (e) through (h) above; thereby depositing a silicon oxide material on said acrylate material.

Optionally, the method further includes:

- (k) dip coating PVDC on the non-ideal barrier coating composition sequence.

Optionally, steps (i) through (j) may be repeated from about 1 to about 20 times before dip coating PVDC on the silicon oxide material.

Optionally, the container and/or the organic material may be flame-treated or plasma oxygen treated or corona discharge treated prior to applying the inorganic material.

Plastic tubes coated with the non-ideal barrier coating sequence composition are able to maintain substantially far

better vacuum retention, draw volume and mechanical integrity retention than previous tubes comprised of polymer compositions and blends thereof without an ideal barrier coating or of tubes comprising only an oxide material. In addition, the tube's resistance to impact is much better than that of glass. Most notably is the clarity of the non-ideal barrier coating sequence composition of the present invention and its durability to substantially withstand resistance to impact and abrasion.

Most preferably, the container of the present invention is a blood collection device. The blood collection device can be either an evacuated blood collection tube or a non-evacuated blood collection tube. The blood collection tube is desirably made of polyethylene terephthalate (PET), polypropylene (PP), polyethylene naphthalate (PEN), polycarbonate (PC) or copolymers thereof.

In addition to blood collection devices, the non-ideal barrier coating sequence composition of the present invention may be used with polymer films wherein both sides of the film include the non-ideal composition of the present invention. Such films may be about 0.002" or less in thickness.

Printing may be placed on the non-ideal barrier coating sequence composition of the present invention. For example, a product identification, bar code, brand name, company logo, lot number, expiration date and other data and information may all be included on the non-ideal composition. Moreover, a matte finish or a corona discharged surface may be developed on the non-ideal composition so as to make the surface appropriate for writing additional information on the label. Furthermore, a pressure sensitive adhesive label may be placed over the non-ideal composition so as to accommodate various hospital over-labels, for example.

Preferably, the non-ideal composition of the present invention provides a transparent or colorless appearance and may have printed matter applied thereon.

An advantage is that the non-ideal composition of the present invention provides a reduction in the gas permeability of three-dimensional objects that has not been achieved with conventional or ideal compositions typically used with thin films.

The non-ideal composition of the present invention provides a reduction in permeation greater than is expected by standard permeation theory. Permeation thermodynamics demonstrates that the non-ideal composition of the present invention exhibits a more nearly "glass-like" property than a single-layer ideal SiO_x composition. Therefore, the non-ideal composition of the present invention provides an unpredicted barrier system.

It has been found that a highly crosslinked layer of acrylate improves the adhesion between a plastic surface and SiO_x and overall improves the thermomechanical stability of the non-ideal barrier coating sequence composition. In addition, the acrylate material covers the particles and imperfections on the surface of a polymer and reduces the defect density in the non-ideal barrier coating sequence composition. The good bonding properties of the acrylate are also due to the fact that acrylate is polar and the polarity provides means for good bond formation between the SiO_x and the acrylate. In addition, it enhances the bond formation between plastic tubes made of polypropylene and SiO_x . Thus, the present invention provides the means of substantially improving the barrier properties of polypropylene tubes.

A plastic blood collection tube coated with the non-ideal barrier coating sequence composition of the present invention will not interfere with testing and analysis that is typically performed on blood in a tube. Such tests include but are not limited to, routine chemical analysis, biological inertness, hematology, blood chemistry, blood typing, toxicology analysis or therapeutic drug monitoring and other clinical tests involving body fluids. Furthermore, a plastic blood collection tube coated with the non-ideal barrier coating sequence composition is capable of being subjected to automated machinery such as centrifuges and may be exposed to certain levels of radiation in the sterilization process with substantially no change in optical or mechanical and functional properties.

It has also been found that the non-ideal barrier coating sequence composition of the present invention does not exhibit true laminate properties in accordance with the laminate equation.

As illustrated in FIG. 1, when two or more different barrier films are stacked, the permeation of small molecules through the multilayer laminate is generally described by the laminate equation:

$$(\Pi_{12}) = (\Pi_1^{-1} + \Pi_2^{-1})^{-1}$$

where Π_1 , is the permeation rate through component layer 1, Π_2 , is the permeation rate through component layer 2 and Π_{12} , is the permeation rate through the laminate of components 1 and 2. When the permeance of the individual components is known, the permeance of the total layer laminate of those components can be calculated and predicted.

However, the transport rate of permeants through the non-ideal barrier coating sequence composition of the present invention is lower than the permeation rate predicted by the laminate equation. Therefore, the non-ideal barrier coating sequence composition of the present invention is a non-ideal composite with unpredicted transport rate of permeants.

The performance of the non-ideal barrier coating sequence composition of the present invention is different from predicted laminates because permeation of gases through the non-ideal barrier coating sequence composition of the present invention requires the expenditure of more thermal energy than would be predicted from the laminate equation.

The laminate equation is therefore modified for the non-ideal barrier coating sequence composition of the present

invention as follows:

$$\Pi_{oi} < (\Pi_o^{-1} + \Pi_i^{-1})^{-1}$$

5 where Π_o is the permeation rate through the organic material of the sequence, Π_i is the permeation rate through the inorganic material of the sequence and Π_{oi} is the permeation rate through the laminate of the organic and inorganic materials. The transport rate of permeants is therefore less than expected from ideal additivity.

It can therefore be concluded that the transport rate of permeants of the non-ideal barrier coating sequence composition or non-ideal composite composition of the present invention is not an additive effect. Therefore, non-ideal composite composites must be discovered for maximum permeance efficiency or performance and not predicted.
10 Furthermore, the permeance properties of a non-ideal composite composition are not inherent.

When the transmission rate of a permeant, such as oxygen or water, through a barrier structure is obtained at several different temperatures, the thermodynamic energy necessary to transport the permeant completely through the barrier structure is obtained by the Arrhenius equation:

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$$\ln Q = \ln Q_o - \Delta G/RT$$

where ΔG is the energy necessary to move one mole of permeant molecules through the barrier structure in cal/mole, R is the gas constant in cal/mole - degree, T is temperature in degrees Kelvin, Q is the permeant transmission rate and Q_o is a constant unique to the structure. In practice, the transmission rate Q for oxygen transport through the barrier structure is obtained at several temperatures. Then the natural log of the transmission rate obtained at each temperature versus the reciprocal of each temperature is plotted. The slope of the resultant linear plot is the quantity $-\Delta G/R$, from which ΔG is obtained.

It has also been found that the non-ideal barrier coating sequence composition of the present invention results in the expenditure of more thermal energy (ΔG) than that of any of the components of the composition or $\Delta G_T > \Delta G_A, \Delta G_B$, where T is the non-ideal barrier coating sequence composition and A and B are the organic and inorganic components of the non-ideal barrier coating sequence composition. In contrast, a laminate or ideal composite composition will have a $\Delta G_T = \Delta G_A$ or ΔG_B , whichever component (A or B) has the lowest permeance.
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30 DESCRIPTION OF THE DRAWINGS

FIG. 1 is a perspective view of a typical blood collection tube with a stopper.

FIG. 2 is a longitudinal sectional view of the tube of FIG. 1 taken along line 2-2.

FIG. 3 is a longitudinal sectional view of a tube-shaped container similar to the tube of FIG. 1 without a stopper,
35 comprising the barrier coating composition.

FIG. 4 is a longitudinal sectional view of a tube-shaped container, similar to the tube of FIG. 1 with a stopper, comprising the barrier coating composition.

FIG. 5 is a longitudinal sectional view of a further embodiment of the invention illustrating the tube with a stopper similar to FIG. 1 and with the barrier coating composition encompassing both the tube and stopper thereof.

40 FIG. 6 illustrates an enlarged partially sectioned, diagram of a flash evaporator apparatus.

FIG. 7 illustrates a plasma deposition system.

FIG. 8 is the plot of the natural log of the transmission rates versus the reciprocal of the temperature for the measurements of Examples 1, 3 and 4 and Table 1.

FIG. 9 illustrates the draw volume loss for PET/[Ac/SiO_x]_n Tubes at 40°C, 1 atm in accordance with the data
45 reported in Table 4.

DETAILED DESCRIPTION

The present invention may be embodied in other specific forms and is not limited to any specific embodiments described in detail which is merely exemplary. Various other modifications will be apparent to and readily made by those skilled in the art without departing from the scope and spirit of the invention. The scope of the invention will be measured by the appended claims and their equivalents.

Referring to the drawings in which like reference characters refer to like parts throughout the several views thereof, FIGS. 1 and 2 show a typical blood collection tube 10, having a sidewall 11 extending from an open end 16 to a closed end 18 and a stopper 14 which includes a lower annular portion or skirt 15 which extends into and presses against the inner surface 12 of the sidewall for maintaining stopper 14 in place.
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FIG. 2 schematically illustrates that there are three mechanisms for a change in vacuum in a blood collection tube: (A) gas permeation through the stopper material; (B) gas permeation through the tube and (C) leak at the stopper tube interface. Therefore, when there is substantially no gas permeation and no leak, there is good vacuum retention and

good draw volume retention.

FIG. 3 shows the preferred embodiment of the invention, a plastic tube coated with a non-ideal barrier coating sequence composition. The preferred embodiment includes many components which are substantially identical to the components of FIGS. 1 and 2. Accordingly, similar components performing similar functions will be numbered identically to those components of FIGS. 1 and 2, except that a suffix "a" will be used to identify those components in FIG. 3.

Referring now to FIG. 3, the preferred embodiment of the invention, collection tube assembly 20 comprises a plastic tube 10a, having a sidewall 11a extending from an opened end 16a to a closed end 18a. A non-ideal barrier coating composition 25 extends over a substantial portion of the outer surface of the tube with the exception of open end 16a. Non-ideal barrier coating sequence composition 25 comprises a sequence of organic and inorganic materials and PVDC.

The sequence composition preferably comprises multiple materials expressed as follows:

$$\text{Sequence} = \sum_n (\text{organic material} + \text{inorganic material})$$

where $n=1-20$.

FIG. 4 illustrates an alternate embodiment of the invention, wherein collection tube assembly 40 comprises stopper 48 in place for closing open end 41 of tube 42. As can be seen, sidewall 43 extends from open end 41 to closed end 44 and stopper 48 includes an annular upper portion 50 which extends over the top edge of tube 42. Stopper 48 includes a lower annular portion or skirt 49 which extends into and presses against the inside inner surface 46 of sidewall 43 for maintaining stopper 48 in place. Also, the stopper has a septum portion 52 for receiving a cannula therethrough.

Thus, the user, once receiving a container such as that shown in FIG. 4 with a sample contained therein, may insert a cannula through septum 52 for receiving part or all of the contents in tube 42 to perform various tests on a sample. Covering a substantial portion of the length of the tube is the non-ideal barrier coating sequence composition 25. Non-ideal barrier coating sequence composition 25 covers substantially most of the tube with the exception of open end 41 thereof. FIG. 4 differs from the embodiment in FIG. 3 in that the tube may be evacuated with the simultaneous placement of stopper 48 therein after the application of non-ideal barrier coating sequence composition 25 over the tube. Alternatively, non-ideal barrier coating sequence composition 25 may be applied to the tube after it has been evacuated.

FIG. 5 shows an additional embodiment of the non-ideal barrier coating sequence composition and a tube. The alternate embodiment functions in a similar manner to the embodiment illustrated in FIG. 4. Accordingly, similar components performing similar functions will be numbered identically to those components in the embodiment of FIG. 4, except that a suffix "a" will be used to identify those components in FIG. 5.

Referring now to FIG. 5, a further embodiment 60 of the invention wherein the non-ideal barrier coating sequence composition 25a incorporates both upper portion 50a of stopper 48a, as well as the entire outer surface of tube 42a. Non-ideal barrier coating sequence composition 25a includes serrations 62 at the tube, stopper interface. The serrations are registered so that it can be determined if the sealed container has been tampered with. Such an embodiment may be utilized, for example, for sealing the container with the stopper in place. Once a sample has been placed in the tube, the sample cannot be tampered with by removal of the stopper. Additionally, the serrations may be registered so that it can be determined if the sealed container has been tampered with. Such an arrangement may be appropriate, for example, in drug abuse testing, specimen identification and quality control.

It will be understood by practitioners-in-the-art, that such tubes may contain reagents in the form of additives or coatings on the inner wall of the tube.

The non-ideal barrier coating sequence composition forms a substantially clear or translucent material. Therefore, the contents of a plastic tube with the non-ideal barrier coating sequence composition is substantially visible to the observer at the same time identifying information may be displayed over the non-ideal barrier coating sequence composition after it is applied to the plastic tube.

The organic material is an acrylate material and may be formed by dip-coating, roll-coating or spraying acrylate monomer or the blend of monomers, followed by UV curing process.

The acrylate material may also be applied by an evaporation and curing process carried out as described in U.S. Patent No. 5,032,461, the disclosure of which is herein incorporated by reference.

The acrylate evaporation and curing process involves first atomizing the acrylate monomer into about 50 micron droplets and then flashing them off of a heated surface. This produces an acrylate molecular vapor which has the same chemistry as the starting monomer.

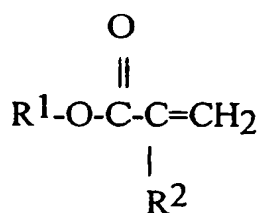
Acrylates are available with almost any chemistry desired. They usually have either one, two or three acrylate groups per molecule. Various mixtures of mono, di and tri acrylates are useful in the present invention. Most preferable are monoacrylates and diacrylates.

Acrylates form one of the most reactive classes of chemicals. They cure rapidly when exposed to UV or electron beam radiation to form a cross-linked structure. Therefore acrylates impart high temperature, stability and abrasion

resistant properties to compositions.

The monomer materials utilized are relatively low in molecular weight, between 150 and 1,000 and preferably in the range of 200 to 300 and have vapor pressures between about 1×10^{-6} Torr and 1×10^{-1} Torr at standard temperature and pressure (i.e., relatively low boiling materials). A vapor pressure of about 1×10^{-2} Torr is preferred. Polyfunctional acrylates are especially preferred. The monomers employed have at least two double bonds (i.e., a plurality of olefinic groups). The high-vapor-pressure monomers used in the present invention can be vaporized at low temperatures and thus are not degraded (cracked) by the heating process. The absence of unreactive degradation products means that films formed from these low molecular weight, high-vapor-pressure monomers have reduced volatile levels of components. As a result, substantially all of the deposited monomer is reactive and will cure to form an integral film when exposed to a source of radiation. These properties make it possible to provide substantially continuous coating despite the fact that the film is very thin. The cured film exhibits excellent adhesion and is resistant to chemical attack by organic solvents and inorganic salts.

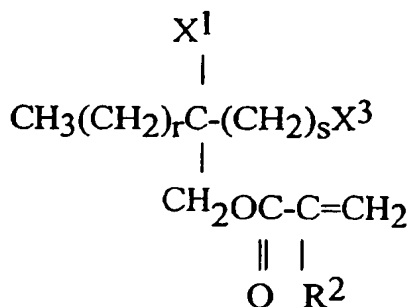
Because of their reactivity, physical properties and the properties of cured films formed from such components, polyfunctional acrylates are particularly useful monomeric materials. The general formula for such polyfunctional acrylates is:



wherein:

R^1 is an aliphatic, alicyclic or mixed aliphatic-alicyclic radical; and
 R^2 is a hydrogen, methyl, ethyl, propyl, butyl or pentyl.

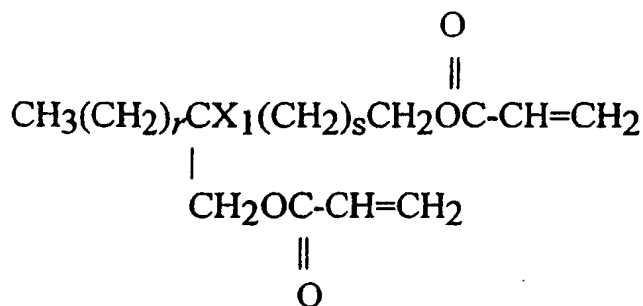
Such polyfunctional acrylates may also be used in combination with various monacrylates, such as those having the formula:



wherein:

R^2 , is as defined above;
 X^1 is H, epoxy, 1,6-hexanediol, tripropyleneglycol or urethane;
 r, s are 1-18; and
 X^3 is CN or COOR^3 .

Diacylates of the formula below are particularly preferred:



wherein:

X_1 , r and s are as defined above.

Curing is accomplished by opening the double bonds of the reactant molecules. This can be accomplished by means of an energy source such as apparatus which emits infrared, electrons or ultraviolet radiation.

FIG. 6 illustrates the process for applying an acrylate material. An acrylate monomer 100 is directed through a dielectric evaporator 102 and then through an ultrasonic atomizer 104 and into a vacuum chamber 106. The monomer droplets are atomized ultrasonically and the droplets vaporized where they condense on the rotating tube or film that is loaded on a drum 108.

The condensed monomer liquid subsequently is radiation cured by means of an electron beam gun 110.

The inorganic material is an oxide material and may be formed by radio frequency discharge, direct or dual ion beam deposition, sputtering or plasma chemical vapor deposition, as described in U.S. Patent Nos. 4,698,256, 4,809,876, 4,992,298 and 5,055,318, the disclosures of which are herein incorporated by reference.

For example, a method of depositing an oxide material is provided by establishing a glow discharge plasma in a previously evacuated chamber. The plasma is derived from one or more gas stream components, and preferably is derived from the gas stream itself. The article is positioned in the plasma, preferably adjacent the confined plasma, and the gas stream is controllably flowed into the plasma. An oxide based film is deposited to a desired thickness. The thickness of the oxide material is about 100 Angstroms (Å) to about 10,000 Å. A thickness of less than about 500 Å may not provide sufficient barrier and a thickness of greater than about 5,000 Å may crack, thus decreasing the effective barrier. Most preferably, the thickness of the oxide material is about 1,000 Å to about 3,000 Å.

Another method of depositing an oxide material is by confining a plasma with magnets. Preferably, the magnetically enhanced method for depositing a silicon oxide based film on a substrate is conducted in a previously evacuated chamber of glow discharge from a gas stream. The gas stream preferably comprises at least two components: a volatilized organosilicon component, an oxidizer component such as oxygen, nitrous oxide, carbon dioxide or air and an optionally inert gas component.

Examples of suitable organosilicon compounds useful for the gas stream in the plasma deposition methods are liquid or gas at about ambient temperature and when volatilized have a boiling point about 0°C to about 150°C and include dimethylsilane, trimethylsilane, diethylsilane, propylsilane, phenylsilane, hexamethyldisilane, 1,1,2,2-tetramethyldisilane, bis (trimethylsilane)methane, bis (dimethylsilyl) methane, hexamethyldisiloxane, vinyl trimethoxy silane, vinyl triethoxysilane, ethylmethoxysilane, ethyltrimethoxysilane, divinyltetramethyldisiloxane, hexamethyldisilazane, divinylhexamethyltrisiloxane, trivinylpentamethyltrisiloxazane, tetraethoxysilane and tetramethoxysilane.

Among the preferred organosilicons are 1,1,3,3-tetramethyldisiloxane, trimethylsilane, hexamethyldisiloxane, vinyltrimethylsilane, methyltrimethoxysilane, vinyltrimethoxysilane and hexamethyldisilazane. These preferred organosilicon compounds have boiling points of 71°C, 55.5°C, 102°C, 123°C and 127°C respectively.

The optional inert gas of the gas stream preferably is helium, argon or nitrogen.

The volatilized organosilicon component is preferably admixed with the oxygen component and the inert gas component before being flowed into the chamber. The quantities of these gases being so admixed are controlled by flow controllers so as to adjustably control the flow rate ratio of the gas stream components.

Various optical methods known in the art may be used to determine the thickness of the deposited film while in the deposition chamber, or the film thickness can be determined after the article is removed from the deposition chamber.

The deposition method of the present invention is preferably practiced at relatively high power and quite low pressure. A pressure less than about 500 millitorr (mTorr) should be maintained during the deposition, and preferably the chamber is at a pressure between about 43 to about 490 millitorr during the deposition of film. Low system pressure results in lower deposition rates whereas higher system pressure provides faster deposition rates. When the plastic article to be coated is heat sensitive, a higher system pressure may be used to minimize the amount of heat the substrate

is exposed to during deposition because high substrate temperatures are to be avoided for low Tg polymers such as polypropylene and PET (Tg is -10°C and 68°C respectively).

The substrate is electrically isolated from the deposition system (except for electrical contact with the plasma) and is at a temperature of less than about 80°C during the depositing. That is, the substrate is not deliberately heated.

Referring to FIG. 7, the system for depositing a silicon oxide material comprises an enclosed reaction chamber 170 in which a plasma is formed and in which a substrate or tube 171, is placed for depositing a thin film of material on a sample holder 172. The substrate can be any vacuum compatible material, such as plastic. One or more gases are supplied to the reaction chamber by a gas supply system 173. An electric field is created by a power supply 174.

The reaction chamber can be of an appropriate type to perform any of the plasma-enhanced chemical vapor deposition (PECVD) or plasma polymerization process. Furthermore, the reaction chamber may be modified so that one or more articles may be coated with an oxide layer simultaneously within the chamber.

The pressure of the chamber is controlled by a mechanical pump 188 connected to chamber 170 by a valve 190.

The tube to be coated is first loaded into chamber 170 in sample holder 172. The pressure of the chamber is reduced to about 5m Torr by mechanical pump 188. The operating pressure of the chamber is about 90 to about 140 mTorr for a PECVD or plasma polymerization process and is achieved by flowing the process gases, oxygen and trimethyl silane, into the chamber through monomer inlet 176.

The thin film is deposited on the outer surface of the tube and has a desired uniform thickness or the deposition process may be interrupted periodically to minimize heating of the substrate and/or electrodes and/or physically remove particulate matter from the articles.

Magnets 196 and 198 are positioned behind electrode 200 to create an appropriate combination of magnetic and electrical fields in the plasma region around the tube.

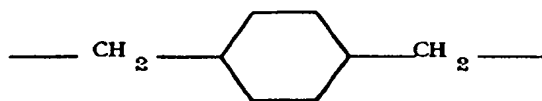
The system is suitable for low frequency operation. An example frequency is 40kHz. However, there can be some advantages from operating at a much high frequency, such as in the radio frequency range of several megahertz.

The oxide materials or blends thereof used in accordance with this disclosure, may contain conventional additives and ingredients which do not adversely affect the properties of articles made therefrom.

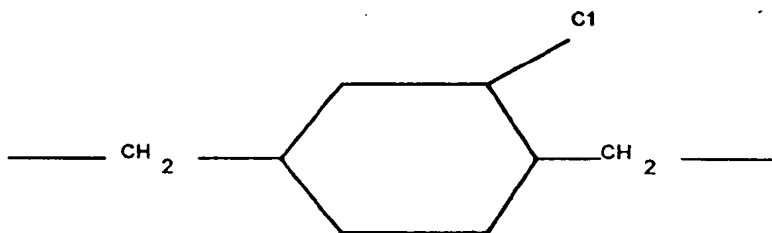
An optional additional material may be formed on the non-ideal barrier coating sequence composition by dip-coating, roll-coating or spraying an aqueous emulsion of the polyvinylidene chloride or homo or co-polymers, followed by air drying.

The optional additional material may preferably be vinylidene chloride-acrylonitrile-methyl methacrylate-methyl acrylate-acrylic acid copolymers, thermosetting epoxy coatings, parylene polymers, or polyesters.

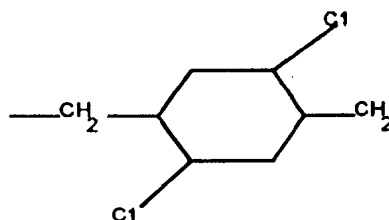
Preferably, the optional additional material is a parylene polymer. Parylene is the generic name for members of the polymer series developed by Union Carbide Corporation. The base member of the series, called parylene N, is poly-p-xylylene, a linear, crystalline material:



Parylene C, a second member of the parylene series is produced from the same monomer as parylene N and modified by the substitution of a chlorine atom for one other aromatic hydrogens:



Parylene D, the third member of the parylene series is produced from the same monomer as parylene N and modified by the substitution of the chlorine atom for two of the aromatic hydrogens:



Most preferably, the polymer material is a vinylidene chloride-methyl methacrylate-methacrylate acrylic acid polymer (PVDC). This polymer is available as DARAN[®] 8600-C (trademark of W.R. Grace and Co.) sold by GRACE, Organic Chemicals Division, Lexington, Mass.

The optional additional material may be a parylene polymer. The optional additional material may be processed similar to vacuum metallizing, as described in U.S. Patent Nos. 3,342,754 and 3,300,332, the disclosures of which are herein incorporated by reference. Alternatively, the optional additional material may be vinylidene chloride-acrylonitrile-methyl methacrylate-methyl acrylate-acrylic acid polymer. This material is applied by dip-coating, roll-coating or spraying an aqueous emulsion of the polymer, followed by air drying of the coating, as described in U.S. Patent Nos. 5,093,194 and 4,497,859, the disclosure of which are herein incorporated by reference.

A variety of substrates can be coated with the non-ideal barrier coating sequence composition by the process of the present invention. Such substrates include, but are not limited to packaging, containers, bottles, jars, tubes and medical devices.

A plastic blood collection tube coated with the non-ideal barrier coating sequence composition will not interfere with testing and analysis that is typically performed on blood in a tube. Such tests include but are not limited to, routine chemical analysis, biological inertness, hematology, blood chemistry, blood typing, toxicology analysis or therapeutic drug monitoring and other clinical tests involving body fluids. Furthermore, a plastic blood collection tube coated with the non-ideal barrier coating sequence composition is capable of being subjected to automated machinery such as centrifuges and may be exposed to certain levels of radiation in the sterilization process with substantially no change in optical or mechanical and functional properties.

A plastic blood collection tube coated with the non-ideal barrier coating sequence composition is able to maintain 90% original draw volume over a period of one year. Draw volume retention depends on the existence of a particle vacuum, or reduced pressure, inside the tube. The draw volume changes in direct proportion to the change in vacuum (pressure). Therefore, draw volume retention is dependent on good vacuum retention. A plastic tube coated with the non-ideal barrier coating sequence composition substantially prevents gas permeation through the tube material so as to maintain and enhance the vacuum retention and draw volume retention of the tube. Plastic tubes without the non-ideal barrier coating sequence composition coating of the present invention may maintain about 90% draw volume for about 2 years.

It will be understood that it makes no difference whether the plastic composite container is evacuated or not evacuated in accordance with this invention. The presence of the non-ideal barrier sequence coating composition on the outer surface of the container has the effect of maintaining the general integrity of the container holding a sample so that it may be properly disposed of without any contamination to the user. Notable is the clarity of the non-ideal barrier coating sequence composition and its abrasion and scratch resistance.

The non-ideal barrier coating sequence composition used in accordance with this disclosure, may contain conventional additives and ingredients which do not adversely affect the properties of articles made therefrom.

The following examples are not limited to any specific embodiment of the invention, but are only exemplary.

EXAMPLE 1

METHOD FOR APPLYING ACRYLATE TO A SUBSTRATE

An acrylate coating was applied to tubes and films (substrates) of various thickness in a chamber wherein Tripropylene Glycol Diacrylate (TPGDA) was fed into the evaporator and was flash vaporized at about 343°C onto the substrate in the chamber and condensed. The condensed monomer film was then E-beam cured by an electron beam gun.

EXAMPLE 2

METHOD FOR APPLYING SiO_x TO A SUBSTRATE

The substrate from Example 1 above was then attached to a holder which fits midway between the electrodes in a

vacuum chamber. The chamber was closed and a mechanical pump was used to achieve a base pressure of about 50 mTorr.

The electrode configuration was internally capacitively coupled with permanent magnets on the backside of the titanium electrodes. This special configuration provided the ability to confine the glow between the electrodes because of the increase in collision probability between electrons and reacting gas molecules. The net result of applying a magnetic field is similar to increasing the power applied to the electrodes, but without the disadvantages of higher bombardment energies and increased substrate heating. The use of magnetron discharge allows operation in the low pressure region and a substantial increase in polymer deposition rate.

The monomer which consists of a mixture of trimethylsilane (TMS) and oxygen was introduced through stainless steel tubing near the electrodes. The gases were mixed in the monomer inlet line before introduction into the chamber. Flow rates were manually controlled by stainless steel metering valves. A power supply operating at an audio frequency of 40 kHz was used to supply power to the electrodes. The system parameters used for thin film deposition of plasma polymerized TMS/O₂ on the substrate were as follows:

Surface Pretreatment:	TMS Flow	= 0 sccm
	Base Pressure	= 50 mTorr
	Oxygen Flow	= 10 sccm
	System Pressure	= 140 mTorr
	Power	= 50 watts
Oxide Deposition:	Time	= 2 minutes
	TMS Flow	= 0.75 - 1.0 sccm
	Oxygen Flow	= 2.5 - 3.0 sccm
	System Pressure	= 90 - 100 mTorr
	Power	= 30 watts
	Deposition Time	= 5 minutes

After the thin film was deposited, the chamber was allowed to cool. The chamber was then opened, and the substrate was removed.

EXAMPLE 3

METHOD FOR APPLYING A NON-IDEAL BARRIER COATING SEQUENCE COMPOSITION TO A SUBSTRATE

A non-ideal barrier coating sequence composition was applied to a substrate by repeating Examples 1 and 2 above from 1 to 20 times.

EXAMPLE 4

METHOD FOR APPLYING ACRYLATE TO A SUBSTRATE

An acrylate coating was applied to tubes and films (substrates) in a chamber wherein a 60:40 mixture of isobornyl acrylate: epoxydiacrylate (IBA:EDA) was fed into the evaporator and flash vaporized at about 343°C onto the substrate in the chamber and condensed. The condensed monomer film was then UV cured by an actinic light source of 365 nm.

EXAMPLE 5

METHOD FOR APPLYING SiO_x TO A SUBSTRATE

The substrate from Example 4 was then attached to a holder which fits midway between the electrodes in a vacuum chamber. The chamber was closed and a mechanical pump was used to achieve a base pressure of about 50 mTorr.

The electrode configuration was internally capacitively coupled with permanent magnets on the backside of the titanium electrodes. The special configuration provided the ability to confine the glow between the electrodes because of

the increase in collision probability between electrons and reacting gas molecules. The net result of applying a magnetic field is similar to increasing the power applied to the electrodes, but without the disadvantages of higher bombardment energies and increased substrate heating. The use of magnetron discharge allows operation in the low pressure region and a substantial increase in polymer deposition rate.

The monomer which consists of a mixture of trimethylsilane (TMS) and oxygen was introduced through stainless steel tubing near the electrodes. The gases were mixed in the monomer inlet line before introduction into the chamber. Flow rates were manually controlled by stainless steel metering valves. A power supply operating at an audio frequency of 40 kHz was used to supply power to the electrodes. The system parameters used for thin film deposition of plasma polymerized TMS/O₂ on the substrate were as follows:

Surface Pretreatment:	TMS Flow	= 0 sccm
	Base Pressure	= 50 mTorr
	Oxygen Flow	= 10 sccm
	System Pressure	= 140 mTorr
	Power	= 50 watts
	Time	= 2 minutes
Oxide Deposition:	TMS Flow	= 0.75 - 1.0 sccm
	Oxygen Flow	= 2.5 - 3.0 sccm
	System Pressure	= 90 - 100 mTorr
	Power	= 30 watts
	Deposition Time	= 5 minutes

After the thin film was deposited, the chamber was allowed to cool. The chamber was then opened, and the substrate was removed.

EXAMPLE 6

METHOD FOR APPLYING A NON-IDEAL BARRIER COATING SEQUENCE COMPOSITION TO A SUBSTRATE

A non-ideal barrier coating sequence composition was applied to a substrate by repeating Examples 4 and 5 above from 1 to 20 times.

EXAMPLE 7

BEHAVIOR CHARACTERISTICS OF NON-IDEAL COMPOSITE COMPOSITIONS

Various different substrates were prepared in accordance with Examples 1-6 above and then the following characteristics and properties were evaluated and the results are reported in Tables 1, 2 and 3 and Figures 8 and 9.

(i) Laminate equation analysis:

When two or more different barrier films are stacked, the permeation of small molecules through the multilayer laminate is generally described by the laminate equation:

$$(\Pi_{12}) = (\Pi_1^{-1} + \Pi_2^{-1})^{-1}$$

or

$$\Pi = (\sum_n [\Pi_n^{-1}])^{-1}$$

where n is the number of layers of different materials deposited as in Example 6 above, Π_1 is the permeation rate through component layer 1, Π_2 is the permeation rate through component layer 2, and Π_{12} is the permeation rate through the laminate of components 1 and 2. The transport rate of a permeant through a laminate barrier system is therefore dependent upon the transport rate of that permeant through each of the laminate's components. When the permeance of the individual components is known, the permeance of the total layer laminate of those components can be calculated and predicted.

The permeance of oxygen or water through such systems can be obtained at defined temperature and driving pressure by use of a MOCON OX-Tran 2000, MOCON T-1000 or MOCON Permatran device.

(ii) Arrhenius relationship analysis:

When the transmission rate of a permeant, such as oxygen or water, through a barrier structure is obtained at several different temperatures, the thermodynamic energy necessary to transport the permeant completely through the barrier structure is obtained by the Arrhenius equation:

$$\ln Q = \ln Q_0 - \Delta G/RT$$

where ΔG is the energy necessary to move one mole of permeant molecules through the barrier structure in cal/mole, R is the gas constant in cal/mole - degree, T is temperature in degrees Kelvin, Q is the permeant transmission rate and Q_0 is a constant unique to the structure. In practice, the transmission rate Q for oxygen transport through the barrier structure is the permeance Π , obtained at several temperatures. Then the natural log of the transmission rate obtained at each temperature versus the reciprocal of each temperature is plotted. The slope of the resultant linear plot is $-\Delta G/R$, from which ΔG is obtained.

These data are obtained at several defined temperatures, using the same equipment as described above. The resulting permeance data (Π) are then treated by the Arrhenius equation, and ΔG values for the laminate are compared to ΔG values obtained for the components of the laminate. An ideal laminate system has a ΔG equivalent to that of the component with the best barrier characteristics. A non-ideal system has a ΔG greater than that of either component.

(iii) Oxygen permeance (OTR):

Film or plaque samples were tested for oxygen permeance (OTR) using a MOCON Ox-TRAN 2/20 (sold by Modern Controls, Inc., 7500 Boone Avenue N., Minneapolis, MN 55428). A single side of the film sample was exposed to 1 atm of 100% oxygen atmosphere. Oxygen permeating through the sample film was entrained in a nitrogen carrier gas stream on the opposite side of the film, and detected by a coulometric sensor. An electrical signal was produced in proportion to the amount of oxygen permeating through the sample. Samples were tested at 30, 35, 40 and 45°C and 0% relative humidity (R.H.). Samples were conditioned for 1 to 20 hours prior to determining oxygen permeance. The results obtained for polycarbonate (PC) and polyethylene terephthalate (PET) are reported in Tables 1 and 3.

Tube samples were tested for oxygen permeance (OTR) using a MOCON Ox-TRAN 1,000 (sold by Modern Controls, Inc., 7500 Boone Avenue N., Minneapolis, MN 55428). A package adapter was used for mounting the tubes in a manner that allowed the outside of the tube to be immersed in a 100% O₂ atmosphere while the inside of tube is flushed with a nitrogen carrier gas. The tubes were then tested at 30°C and 50% R.H. The tubes were allowed to equilibrate for 2-14 days before a steady state permeability is determined. The results for polyester based blood collection tubes is reported in Table 4, and the results for polypropylene based blood collection tubes is reported in Table 5.

(iv) Water Vapor Transmission Rate (WVTR):

a. Tubes: Tubes were filled with a 2 ml of distilled water, closed with a rubber stopper, and placed into an oven at 40°C, 50% R.H. The tubes were then weighed once a week for 4 months. The water vapor transmission rates were then calculated based on the equilibrium water loss per day. Examples of PET based blood collection tubes are reported in Table 4.

b. Films: Films were placed into the Permatran W-600 instrument at 40°C. A single side of the film was exposed to 100% relative humidity (RH). Water vapor permeating through the sample film was introduced into an IR sensor by a nitrogen carrier gas. An electrical signal was produced in proportion to the amount of water vapor permeating through the sample. Data was collected at 25, 30 and 35°C for use in the Arrhenius equation, $\ln Q = \ln Q_0 - \Delta G/RT$.

A. Non-Ideal Barrier Coating Sequence Compositions on Films

Samples 1-4 of Table 1 and Figure 8 illustrate that coating both sides of a PET film results in an unexpected decrease in the oxygen transmission rate that the laminate equation does not predict. The measured and predicted oxy-

gen transport rate of films coated with SiO_x were compared to the separately measured oxygen transport rate of PET and SiO_x . The results are reported in Figure 8 and Table 1. This occurs despite the fact that the PET/ SiO_x sample behaved as a predictable laminate.

Figure 8 is the Arrhenius equation plot of the natural log of the transmission rates versus the reciprocal of the temperature at which each measurement was taken for Samples 1, 3 and 4. From Figure 8 ΔG , or the energy required to transport one mole of oxygen through $\text{SiO}_x/\text{PET}/\text{SiO}_x$, Sample 4, is 20 ± 1 kcal/mole as compared to the ΔG of 7 ± 2 kcal/mole for PET, Sample 1 and PET/ SiO_x , Sample 3.

This result shows that the non-ideal barrier coating composition of $\text{SiO}_x/\text{PET}/\text{SiO}_x$ results in the expenditure of more thermal energy, ΔG than the individual components of the composition. This is consistent with the relationship of the non-ideal barrier sequence coating composition of the present invention, $\Delta G_T > \Delta G_A, \Delta G_B$, where T is Sample 4 and A and B are Samples 1 and 2 respectively.

Samples 1, 2 and 3 illustrate that PET/ SiO_x , Sample 3 acts only as a laminate of PET and SiO_x , which can be predicted, wherein $\text{SiO}_x/\text{PET}/\text{SiO}_x$, Sample 4 exhibits non-ideal permeance results. Therefore this illustrates that the barrier performance of Sample 4 as a whole is independent of the properties of its constituents, with respect to oxygen permeation.

In addition, Table 2 illustrates the unexpected increase in water vapor barrier performance of Sample 9 ($\text{SiO}_x/\text{PET}/\text{SiO}_x$). The observed water vapor transmission rate through the structure is 30 to 50 times lower than the value predicted from laminate theory, based on the transmission rates through Sample 5 (PET film), Sample 6 (SiO_x) and Sample 7 (PET/ SiO_x).

Samples 10-18 of Table 3 illustrate that the oxygen permeance of PC/ SiO_x /acrylate/ SiO_x (Sample 16) is 1.1×10^{-10} moles/ $\text{m}^2 \cdot \text{sec} \cdot \text{atm}$ as compared to the 16.4×10^{-10} moles/ $\text{m}^2 \cdot \text{sec} \cdot \text{atm}$ that is predicted (Sample 18) with the laminate equation.

In addition, Samples 10-16 also illustrate that the water permeance of PC/ SiO_x /acrylate/ SiO_x (Sample 16) is 0.9×10^{-10} moles/ $\text{m}^2 \cdot \text{sec} \cdot \text{atm}$ as compared to the 4.9×10^{-10} moles/ $\text{m}^2 \cdot \text{sec} \cdot \text{atm}$ predicted (Sample 18) with the laminate equation. The result of Sample 16 shows that the barrier performance of the non-ideal barrier coating sequence composition of PC/ SiO_x /acrylate/ SiO_x as a whole is greater than the sum of each individual material in the whole composition, with respect to both oxygen and water.

Also noted is that Sample 15 (PC/acrylate/ SiO_x) (measured) behaved as a single laminate which indicates that Sample 16 (PC/ SiO_x /acrylate/ SiO_x) should have also exhibited simple laminate characteristics. However, as shown in Table 3, Sample 16, (PC/ SiO_x /acrylate/ SiO_x) did not exhibit simple laminate characteristics. Therefore, it can be concluded that Sample 16 follows the modified laminate equation for a non-ideal barrier coating sequence composition of

$$(\Pi_{\text{PC}/\text{SiO}_x/\text{acrylate}/\text{SiO}_x})^{-1} < (\Pi_{\text{PC}})^{-1} + (\Pi_{\text{acrylate}})^{-1} + 2 (\Pi_{\text{SiO}_x})^{-1}$$

where $(\Pi_{\text{PC}})^{-1}$ is Sample 10, $(\Pi_{\text{acrylate}})^{-1}$ is Sample 12, and

$$(\Pi_{\text{SiO}_x})^{-1}$$

is Sample 11.

Consistent with the laminate characteristics of Sample 16 (PC/ SiO_x /acrylate/ SiO_x) are the ΔG values (energy necessary to transport oxygen or water through the sample) observed for this sample. The ΔG value for oxygen transport through Sample 16, (PC/ SiO_x /acrylate/ SiO_x), is 9 kcal/mole higher than the energy necessary to transport one mole of oxygen through the PC, PC/ SiO_x or PC/acrylate/ SiO_x systems (Samples 10, 14 and 15). This result shows that the non-ideal barrier coating sequence composition results in the expenditure of more thermal energy, ΔG , than any of the components of the composition. This is consistent with the relationship of $\Delta G_T > \Delta G_A, \Delta G_B, \Delta G_C$ where T is Sample 16 and A, B and C are Samples 10, 14 or 15, respectively.

The ΔG value for water transport through Sample 16 follow the same non-ideal characteristics as reported for oxygen transport. The ΔG values for transport through PC/ SiO_x and PC/acrylate/ SiO_x , are 3-4 kcal/mole higher than the ΔG of transport through PC alone. However, the water transmission rate through the PC/ SiO_x /acrylate/ SiO_x structure is not predicted by the laminate equation as compared to Sample 18. These non-ideal results show an unexpected enhancements of water vapor barrier and that $\Delta G_T > \Delta G_A, \Delta G_B, \Delta G_C$ where T is Sample 16 and A, B and C are Samples 10, 14 and 15 respectively.

B. Non-Ideal Barrier Coating Sequence Compositions on Tubes

In addition, an unexpected improvement in barrier properties for PET and PP coated tubes was observed. Tables 4 and 5 summarize the barrier characteristics of PET and PP tubes coated with (acrylate/SiO_x)_n.

Samples 19-27 (Table 5) illustrate that PET tubes coated with more than 1 sequence of acrylate/SiO_x exhibit non-ideal behavior with respect to oxygen and water vapor permeance, wherein experimental water vapor and oxygen transmission rates are significantly lower than theoretically predicted based on the laminate equation.

Samples 25-27 follow the modified laminate equation for a non-ideal barrier coating sequence composition as follows:

$$\Pi_{\text{PET (acrylate/SiO}_x)_n} < ((\Pi_{\text{PET}})^{-1} + n(\Pi_{\text{acrylate}})^{-1} + n(\Pi_{\text{SiO}_x})^{-1})^{-1}$$

where PET (acrylate/SiO_x)_n is Samples 22-25, PET is Sample 19 and acrylate is Sample 23 and SiO_x is Sample 22.

It is observed that the deposition of a single sequence of acrylate/SiO_x does not improve water barrier properties of the PET tube, however, two sequences of acrylate/SiO_x (Sample 25) result in decreasing water vapor transmission rates by a factor of 17.5 compared to the PET control (Sample 19). As a result of a non-ideal barrier behavior, tubes coated with 4 and 6 sequences of acrylate/SiO_x have remarkably low oxygen and water vapor permeance, superior to any transparent barrier coating on a plastic substrate reported in the literature as shown in Table 6.

In addition, Samples 28-33 (Table 5) illustrate non-ideal behavior of the PP tubes coated with 2 sequences of acrylate/SiO_x. The measured oxygen permeance of PP/(acrylate/SiO_x)₂ sequence (Sample 33) is 11.5 x 10⁻¹⁰ moles/m² · sec · atm, compared to 496 x 10⁻¹⁰ moles/m² · sec · atm predicted with the laminate equation. Therefore, it can be concluded that Sample 31 follows the modified laminate equation for a non-ideal barrier coating sequence composition of

$$\Pi_{\text{PP/(acrylate/SiO}_x)_2} < (\Pi_{\text{PP}})^{-1} + 2(\Pi_{\text{acrylate}})^{-1} + 2(\Pi_{\text{SiO}_x})^{-1}$$

where PP/(acrylate/SiO_x)₂ is Sample 33, PP is Sample 28, acrylate is Sample 32 and SiO_x is Sample 30.

TABLE I
BARRIER CHARACTERISTICS OF FILMS

TABLE I BARRIER CHARACTERISTICS OF FILMS								
		Oxygen Transport Rate			Oxygen Permeance			
Sample No.	Sample Description	Q measured 10 ⁻¹⁰ mole/m ² · sec·atm @ 30°C	Q predicted (6) 10 ⁻¹⁰ mole/m ² · sec·atm @ 30°C	ΔG kcal/mole @30°C	Barrier Type	Π _{O₂} @ 33°C (10 ⁻¹⁰ mole/ m ² ·sec·atm)	Π _{O₂} @ 40°C (10 ⁻¹⁰ mole/m ² ·sec·atm)	Π _{O₂} @ 45°C (10 ⁻¹⁰ mole m ² ·sec·atm)
1	PET film	403	..	7+2	Monolithic(1)			
2	SiO _x	2.73	..		Monolithic(1)			
3	PET/SiO _x	2.71	2.71	7+2	Laminate(2)	3.59 (4)	4.28 (4)	5.17 (4)
4	SiO _x /PET/SiO _x	0.56	1.35	20+1	Composite(3)	0.53 (5)	0.91 (5)	1.36 (5)

(1) Monolithic = single component barrier

(2) Laminate = two component barrier with ideal characteristics

(3) Composite = two component barrier with non-ideal characteristics

(4) Π⁻¹ = Π⁻¹_{PET} + Π⁻¹_{SiO_x}

(5) Π⁻¹ < Π⁻¹_{PET} + 2Π⁻¹_{SiO_x} (composite)

TABLE 2
BARRIER CHARACTERISTICS OF FILMS

Sample No.	Sample Description	Water Vapor Transmission Rates (10^{-7} Mole/m ² . sec)			
		25°	30°	35°	40°
5	PET film	153	212	318	424
6	SiO _x	14.6	21.1	30.2	75.4
7	PET/SiO _x	13.31	19.16	27.58	63.98
8	SiO _x /PET/SiO _x (observed)	0.239	0.289	0.450	0.64
9	SiO _x /PET/SiO _x (1)	7.0	10.0	14.4	34.6

(1) predicted from laminate equation: $(\Pi_{\text{SiO}_x/\text{PET/SiO}_x})^{-1} = (\Pi_{\text{PET}})^{-1} + 2(\Pi_{\text{SiO}_x})^{-1}$

TABLE 3
BARRIER CHARACTERISTICS OF FILMS

Sample No.	Sample Description	O ₂ transmission rate (10 ⁻¹⁰ mole/m ² ·sec·atm)	H ₂ O vapor transmission rate 10 ⁻¹⁰ (mole/m ² ·sec·atm)	ΔG _{O₂} (kcal/mole)	ΔG _{H₂O} (kcal/mole)
10	PC film	723.8	252.7	4.4 ± 0.16	9.8 ± 0.29
11	SiO _x	31.2	9.7		
12	acrylate	4818.6	>15,000		
13	PC/acrylate	2893.5	249.5		
14	PC/SiO _x	31.0	9.3	4.2 ± 0.20	13.1 ± 1.10
15	PC/acrylate/SiO _x (measured)	34.9	9.7	4.6 ± 0.30	12.8 ± 0.9
16	PC/SiO _x /acrylate/SiO _x (measured)	1.1	0.9	13.3 ± 2.0	14.6 ± 1.71
17	PC/acrylate/SiO _x (predicted) (1)	33.7	9.7		
18	PC/SiO _x /acrylate/SiO _x (predicted) (2)	16.4	4.9		

(1) Predicted by: $\Pi^{-1} = \Pi^{-1}_{pc} + \Pi^{-1}_{acrylate} + \Pi^{-1}_{SiO_x}$ (sample 17)

(2) Predicted by: $\Pi^{-1} = \Pi^{-1}_{pc} + \Pi^{-1}_{acrylate} + 2\Pi^{-1}_{SiO_x}$ (sample 18)

TABLE 4
BARRIER CHARACTERISTICS OF TUBES

Sample No.	WATER VAPOR TRANSMISSION			OXYGEN PERMEANCE		
	Sample Description	Measured Water Vapor Transmission Rate (10^{-10} moles/m ² ·sec @ 40°C, 50% R.H.)	Theoretical Water Vapor Transmission Rate (10^{-10} moles/m ² ·sec @ 40°C, 50% R.H.)	Measured Oxygen Transmission Rate (10^{-10} mole/m ² ·sec·atm @ 40°C, 0% R.H.)	Theoretical Oxygen Transmission Rate (10^{-10} mole/m ² ·sec·atm @ 40°C, 0% R.H.)	Barrier Type
19	PET tube, control	369		67.8	--	Monolithic
20	PET/SiO _x	370		67.2	--	
21	PET/acrylate	370		67.4	--	
22	SiO _x	135,000				
23	acrylate	137,000				
24	PET (acrylate/SiO _x)1 (1)	370	370	66.6	66.8	Laminate
25	PET (acrylate/SiO _x)2 (2)	101	370	3.8	66.6	Laminate
26	PET (acrylate/SiO _x)4 (3)	64.5	370	1.9	65.5	Laminate
27	PET (acrylate/SiO _x)6 (4)	24.7	370	--	--	Laminate

- (1) 1 sequence of acrylate/SiO_x
 (2) 2 sequences of acrylate/SiO_x
 (3) 4 sequences of acrylate/SiO_x
 (4) 6 sequences of acrylate/SiO_x

TABLE 5

BARRIER CHARACTERISTICS OF TUBES			
Sample No.	Sample Description	Measured Oxygen Transmission Rate (10^{-10} moles/m ² · sec atm)	Theoretical Oxygen Transmission Rate (10^{-10} moles/m ² · sec atm)
28	PP tube, control ⁽¹⁾	1120	
29	PP/SiO _x	1000	
30	SiO _x	9300	
31	PP/acrylate	739.5	--
32	acrylate	2200	--
33	PP/(acrylate/SiO _x) ₂ ⁽²⁾	11.5	496

⁽¹⁾ 1 sequence of acrylate/SiO_x

⁽²⁾ 2 sequences of acrylate/SiO_x

TABLE 6

Reference
Proc. Int. Conf. Vac. Web. Coat, 5th, 123-127, Italy
JP 4904169
Proc. Int. Conf. Vac. Web. Coat. 5th, 86-103
JP No. 91-277164
JP No. 04103757 A2
EP No. 469926 A1
US Patent No. 3,442,686
US Patent No. 4,702,963
US Patent No. 4,557,946

Claims

1. A non-ideal barrier coating sequence composition comprising organic and inorganic materials wherein the barrier performance of said composition as a whole is greater than the lamination of said organic and inorganic materials in said composition.
2. The composition of Claim 1, wherein the permeation rate of the lamination of said organic and inorganic materials (Π_o), is less than the inverse of the sum of the inverse of the permeation rate through said inorganic material (Π_i) of said sequence and the inverse of the permeation rate through said organic material (Π_o) of said sequence.
3. The composition of Claim 2, wherein said permeation rate of the lamination of said organic and inorganic materials is not an additive effect.
4. The composition of Claim 1, wherein the thermal energy (ΔG_T) of said non-ideal barrier coating sequence composition is greater than the thermal energy of said organic component (ΔG_A) and said inorganic component (ΔG_B).

5. The composition of Claim 1, wherein said organic material is a highly crossed linked acrylate or acrylic polymer.
6. The composition of Claim 1, wherein the inorganic material is a metal oxide.
7. The composition of Claim 6, wherein said metal oxide is a silicon oxide based composition or an aluminium oxide based composition.
8. The composition of Claim 7, wherein said silicon oxide based composition is silicon oxide, SiO_x , where x is from about 1.0 to about 2.5.
9. The composition of Claim 5, wherein the thickness of said organic material is about 0.1 microns to about 10 microns.
10. The composition of Claim 9, wherein the thickness of said organic material is about 0.5 microns to about 3 microns.
11. The composition of Claim 6, wherein the thickness of said metal oxide is about 100 to about 2,000 Angstroms.
12. The composition of Claim 11, wherein the thickness of said metal oxide is about 500 to about 1,000 Angstroms.
13. The composition of Claim 1 further comprising poly(vinylidene chloride), thermosetting materials, parylene polymers or polyesters.
14. The composition of Claim 13, wherein said thickness of said poly(vinylidene chloride) is about 2 to about 15 microns.
15. The composition of Claim 14, wherein said thickness of said poly(vinylidene chloride) is about 3 to about 5 microns.
16. A non-ideal barrier coating sequence composition comprising the following sequence:

$$\sum_n (\text{organic material} + \text{inorganic material})$$

where $n=1-20$

17. The composition of Claim 16, wherein the permeation rate of the lamination of said organic and inorganic materials (Π_o), is less than the inverse of the sum of the inverse of the permeation rate through said inorganic material (Π_i) of said sequence and the inverse of the permeation rate through said organic material (Π_o) of said sequence.
18. The composition of Claim 17, wherein said permeation rate of said lamination of said organic and inorganic materials is not an additive effect.
19. The composition of Claim 16, wherein the thermal energy (ΔG_T) of said non-ideal barrier coating sequence composition is greater than the thermal energy of said organic component (ΔG_A) and said inorganic component (ΔG_B).
20. The composition of Claim 16, wherein said organic material is a highly crossed linked acrylate or acrylic polymer.
21. The composition of Claim 16, wherein the inorganic material is a metal oxide.
22. The composition of Claim 21, wherein said metal oxide is a silicon oxide based composition or an aluminum oxide based composition.
23. The composition of Claim 22, wherein said silicon oxide based composition is silicon oxide, SiO_x , where x is from about 1.0 to about 2.5.
24. The composition of Claim 20, wherein the thickness of said organic material is about 0.1 microns to about 10 microns.
25. The composition of Claim 24, wherein the thickness of said organic material is about 0.5 microns to about 3

microns.

26. The composition of Claim 21, wherein the thickness of said metal oxide is about 100 to about 2,000 Angstroms.

27. The composition of Claim 26, wherein the thickness of said metal oxide is about 500 to about 1,000 Angstroms.

28. The composition of Claim 16, further comprising poly(vinylidene chloride), thermosetting materials, parylene polymers or polyesters.

29. The composition of Claim 28, wherein said thickness of said poly(vinylidene chloride) is about 2 to about 15 microns.

30. The composition of Claim 29 wherein said thickness of said poly(vinylidene chloride) is about 3 to about 5 microns.

31. A sample assembly comprising:

a plastic container having an open end, a closed end, an inner surface and an outer surface; and
a non-ideal barrier coating sequence associated over the outer surface of said container composition comprising:

$$\sum_n (\text{organic material} + \text{inorganic material})$$

where $n=1-20$

32. The assembly of Claim 31, wherein the permeation rate of the lamination of said organic and inorganic materials (Π_o) of said sequence, is less than the inverse of the sum of the inverse of the permeation rate through said inorganic material (Π_i) of said sequence and the inverse of the permeation rate through said organic material (Π_o) of said sequence.

33. The assembly of Claim 32, wherein said permeation rate of said lamination of said organic and inorganic materials is not an additive effect.

34. The assembly of Claim 31, wherein said organic material is a polymerized blend of mono-and di-acrylates.

35. The assembly of Claim 31, wherein said inorganic material is aluminium oxide or silicon oxide based composition.

36. The assembly of Claim 31, wherein said organic material comprises polymerized acrylate and said inorganic material comprises silicon oxide.

37. The assembly of Claim 31, wherein said acrylate of said organic material is deposited on said outer surface of said container in a previously evacuated chamber comprising the following steps:

- (a) metering a curable monomer component into a heated vaporizer system;
- (b) flash vaporizing said component in said chamber;
- (c) condensing, vaporizing or atomizing a film of the component onto the outer surface of said container; and
- (d) curing said film.

38. The assembly of Claim 37, wherein said inorganic material is deposited in said previously evacuated chamber onto said organic material by the following steps:

- (a) vaporizing an organosilicon component and admixing the volatilized organosilicon component with an oxidizer component and optionally an inert gas component to form a gas stream exterior to the chamber;
- (b) establishing a glow discharge plasma in the chamber from one or more of the gas stream components;
- (c) controllably flowing the gas stream into the plasma while confining at least a portion of the plasma therein; and
- (d) depositing a layer of silicon oxide adjacent said first layer.

39. The assembly of Claim 38, wherein said oxidizer component is oxygen nitrous oxide, carbon dioxide, air, or an inert compound.
40. The assembly of Claim 39, wherein the plastic substrate is electrically isolated from the chamber except for contact with the confined plasma.
41. The assembly of Claim 40, wherein said sequence further comprises a parylene polymer material.
42. The assembly of Claim 41, wherein said parylene polymer is parylene N, parylene C or parylene D.
43. The assembly of Claim 31, wherein the thermal energy (ΔG_T) of said non-ideal barrier coating sequence composition is greater than the thermal energy of said organic component (ΔG_A) and said inorganic component (ΔG_B).
44. The assembly of Claim 31, wherein said organic material is a highly crossed linked acrylate or acrylic polymer.
45. The assembly of Claim 31, wherein the inorganic material is a metal oxide.
46. The assembly of Claim 45, wherein said metal oxide is a silicon oxide based composition or an aluminum oxide based composition.
47. The assembly of Claim 46, wherein said silicon oxide based composition is silicon oxide, SiO_x , where x is from about 1.0 to about 2.5.
48. The assembly of Claim 45, wherein the thickness of said inorganic material is about 0.1 microns to about 10 microns.
49. The assembly of Claim 48, wherein the thickness of said inorganic material is about 0.5 microns to about 3 microns.
50. The assembly of Claim 45, wherein the thickness of said metal oxide is about 100 to about 2,000 Angstroms.
51. The assembly of Claim 50, wherein the thickness of said metal oxide is about 500 to about 1,000 Angstroms.
52. The assembly of Claim 31, further comprising poly(vinylidene chloride), thermosetting materials, parylene polymers or polyesters.
53. The assembly of Claim 52, wherein said thickness of said poly(vinylidene chloride) is about 2 to about 15 microns.
54. The assembly of Claim 53, wherein said thickness of said poly(vinylidene chloride) is about 3 to about 5 microns.
55. A method of depositing a non-ideal barrier coating sequence composition on a substrate comprising:
 - (a) selecting a curable component comprising: i) polyfunctional acrylates, or ii) mixtures of monoacrylates and polyfunctional acrylates;
 - (b) flash vaporizing said component into said chamber;
 - (c) condensing an acrylate material of said vaporized component onto the outer surface of said substrate;
 - (d) curing said acrylate material;
 - (e) vaporizing an organosilicon component and admixing a volatilized organosilicon component with an oxidizer component and optionally an inert gas component to form a gas stream exterior to the chamber;
 - (f) establishing a glow discharge plasma in the chamber from one or more of the gas stream components;
 - (g) controllably flowing the gas stream into the plasma while confining at least a portion of the plasma therein;
 - (h) depositing a material of silicon oxide adjacent said acrylate material;
 - (i) repeating steps (a) through (d) above, thereby depositing an acrylate material on said silicon oxide material; and
 - (j) repeating steps (e) through (h) above, thereby depositing a silicon oxide material on said acrylate material.
56. The method of Claim 55 further comprising:
 - (k) dip coating PVDC on said non-ideal barrier coating composition sequence.

57. The method of Claim 55 further comprising:

(k) repeating steps (i) through (j) from about 2 to about 20 times.

5 **58.** The method of Claim 57 further comprising:

(l) dip coating PVDC on said non-ideal barrier coating composition sequences.

59. The method of Claim 55 wherein said acrylate material is pretreated by oxygen plasma.

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FIG-1

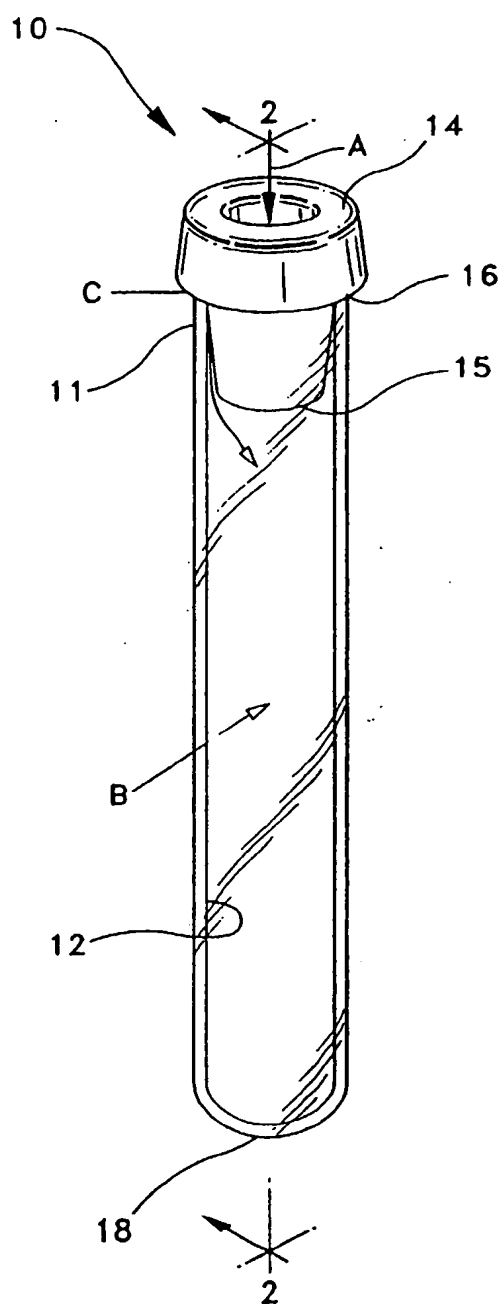


FIG-2

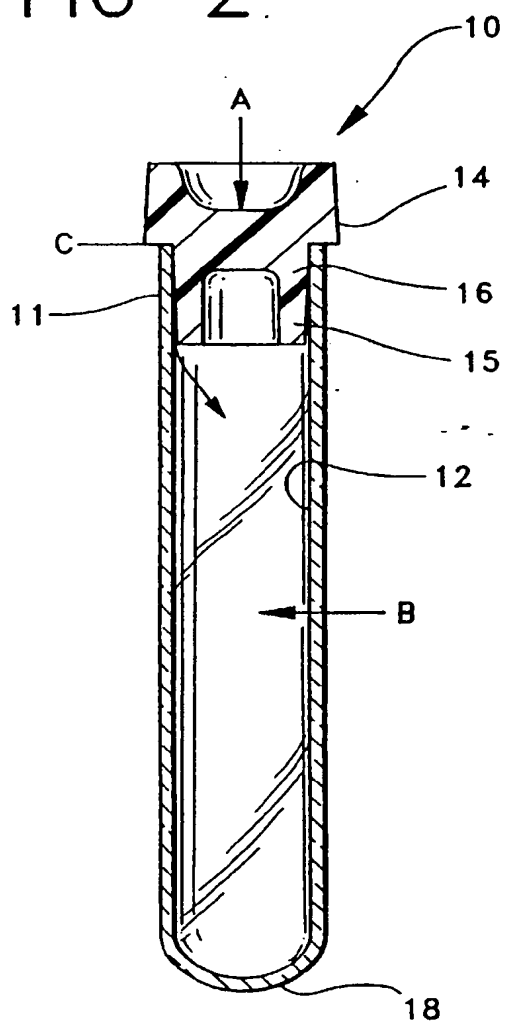


FIG-3

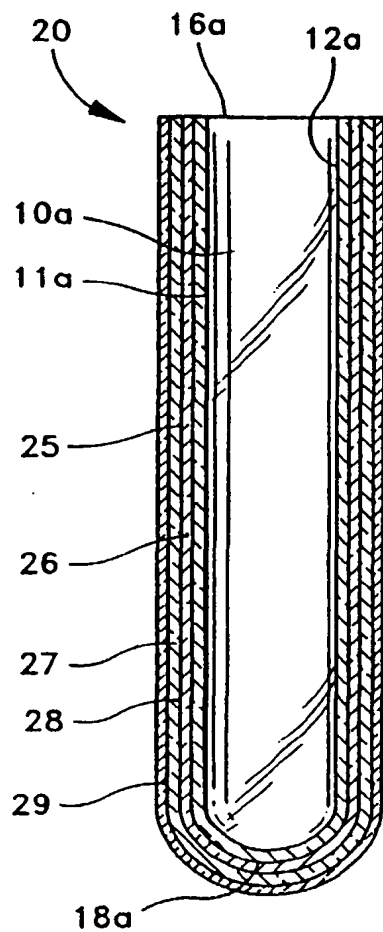


FIG-4

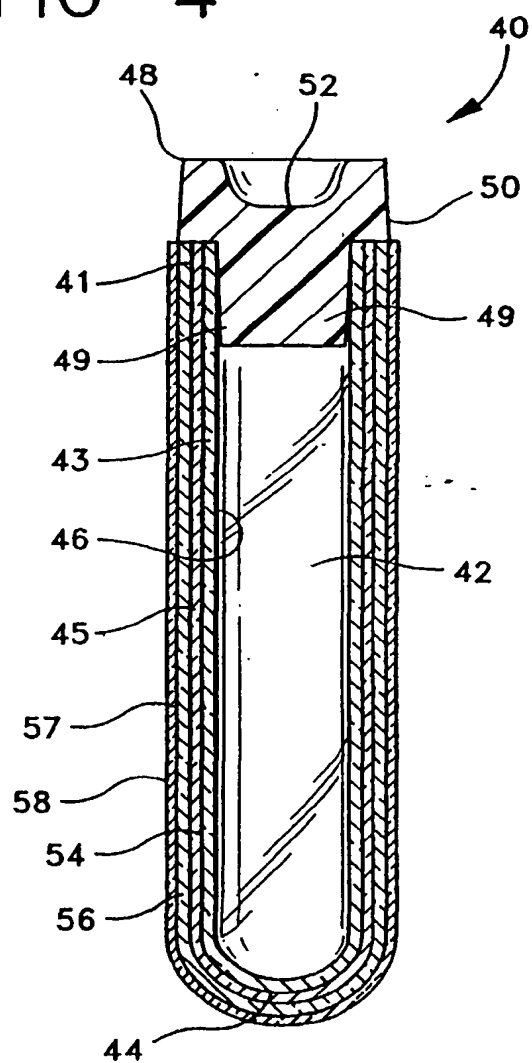


FIG-5

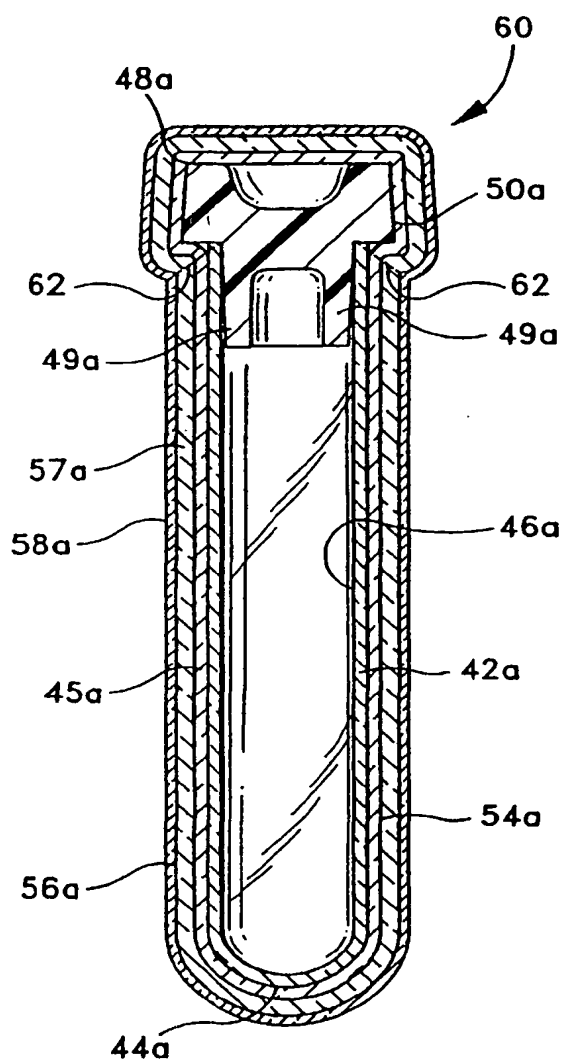


FIG-6

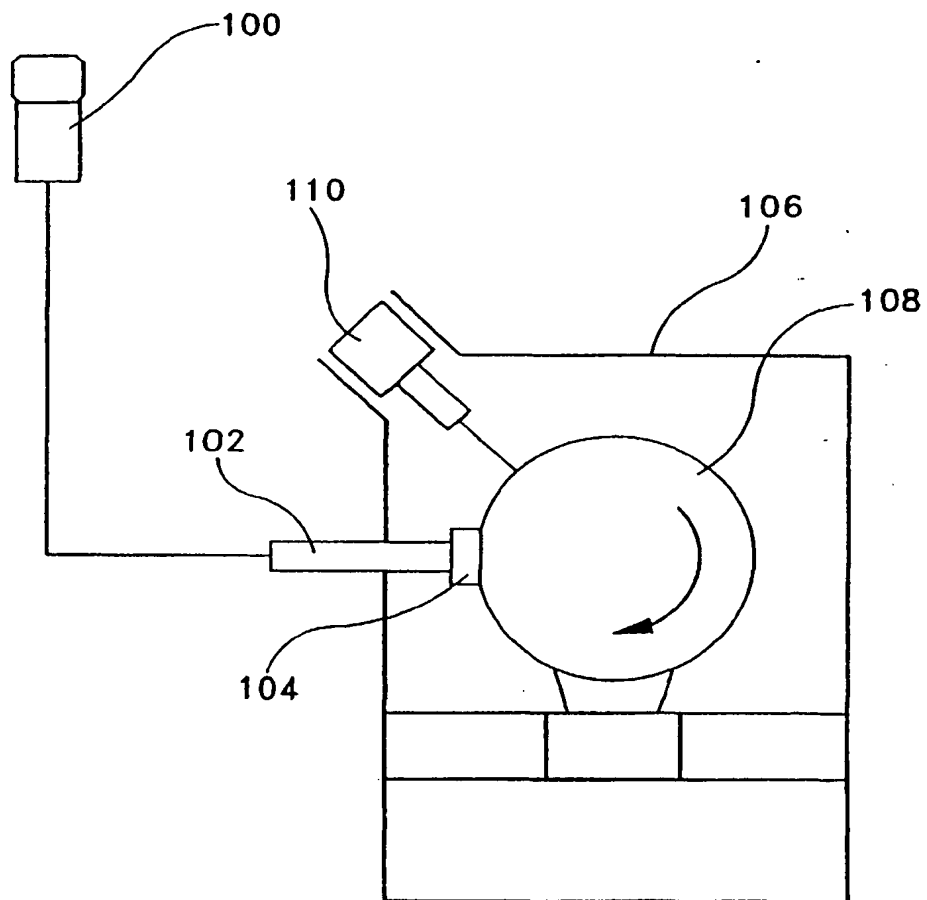


FIG-7

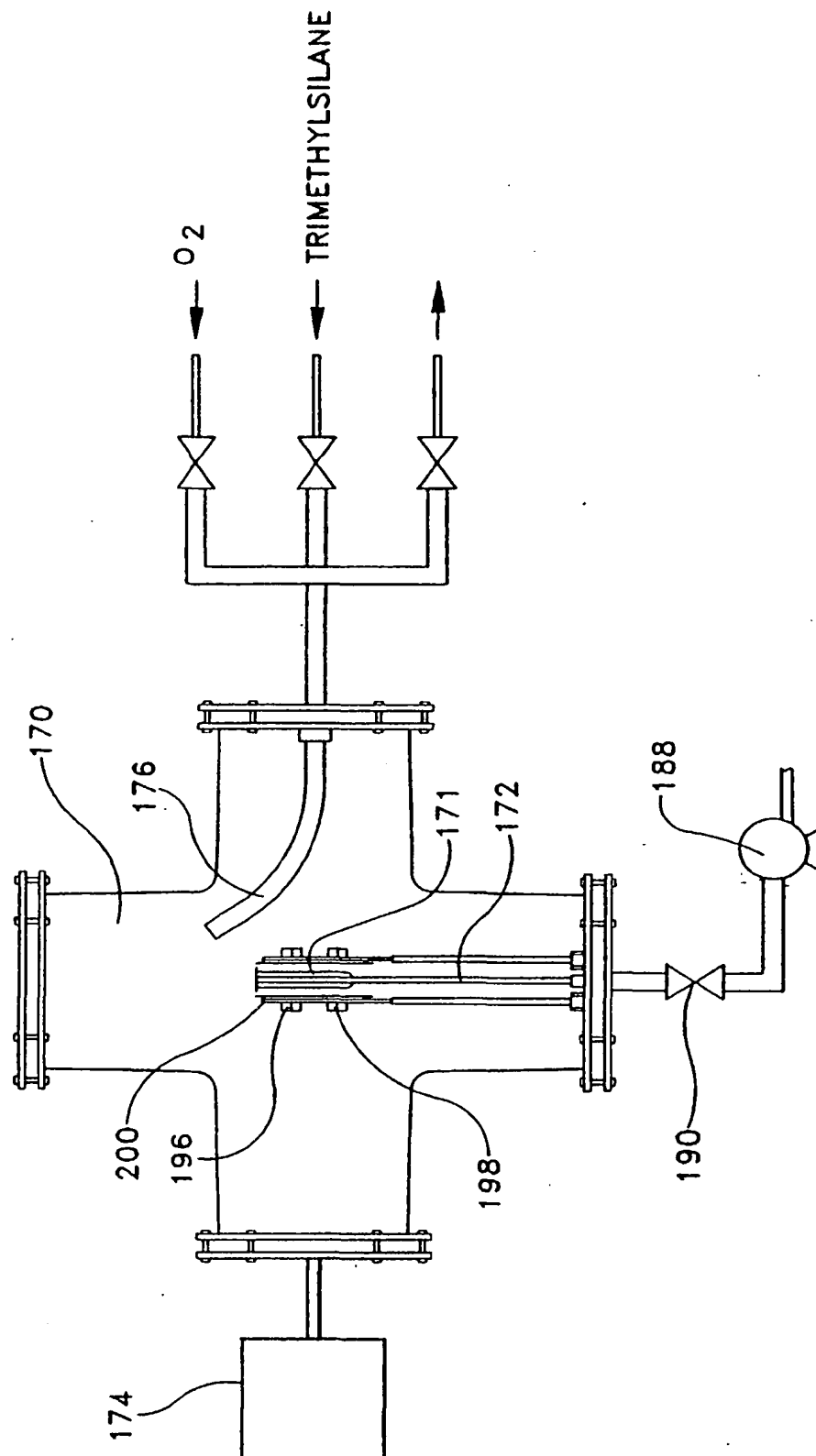


FIG-8 ARRHENIUS PLOT OF OXYGEN TRANSPORT THROUGH PET, PET/SiO_x, AND SiO_x/PET/SiO_x BARRIER FILMS

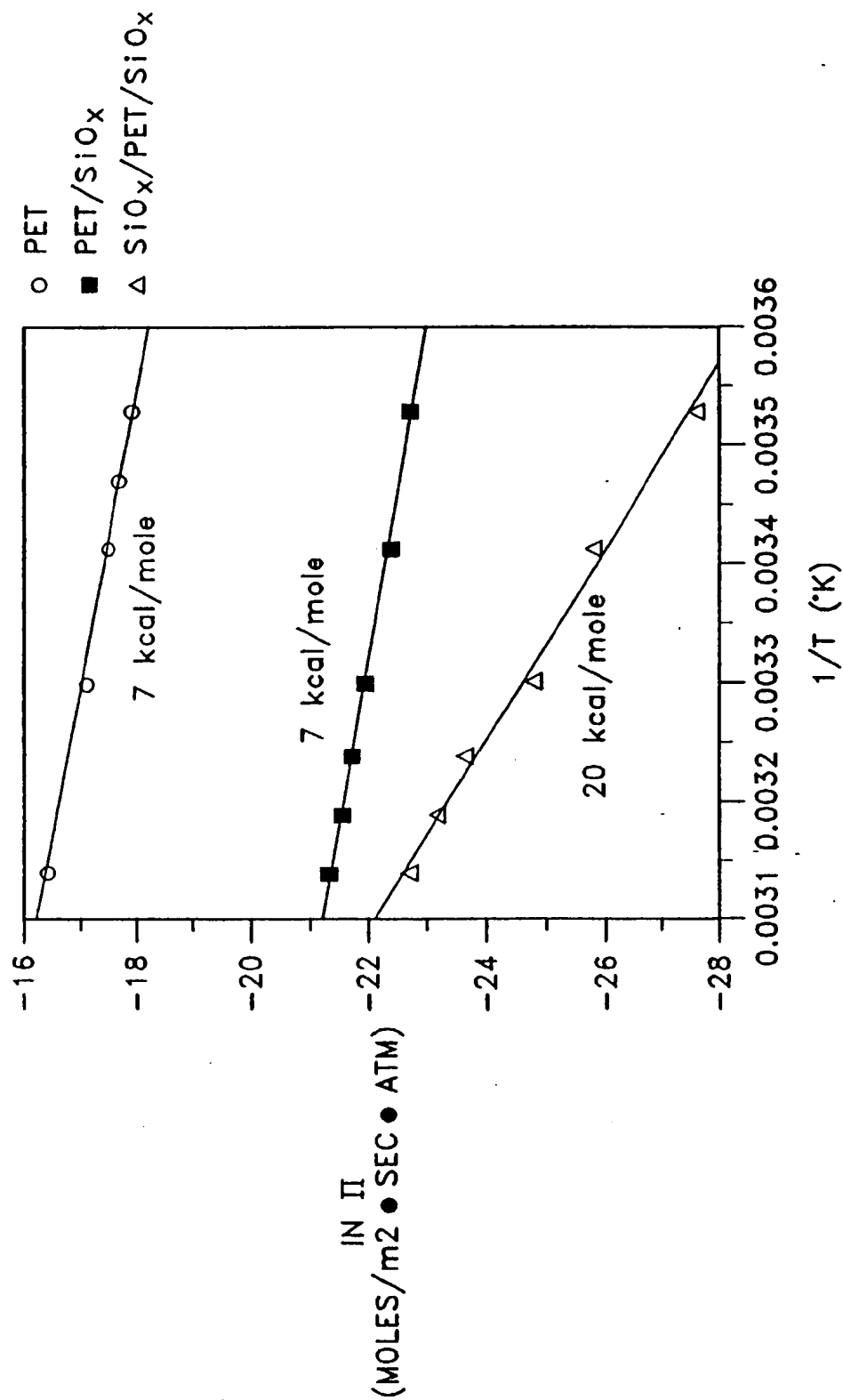


FIG-9

DRAW VOLUME LOSS FOR
PET/[Ac/SiO_x]_n TUBES AT 40°C, 1 ATM

n	DRAW LOSS (% PER YEAR)	SHELF LIFE (MONTHS)
0	41	2.9
1	41	2.9
2	17	7.9
4	12	13.7

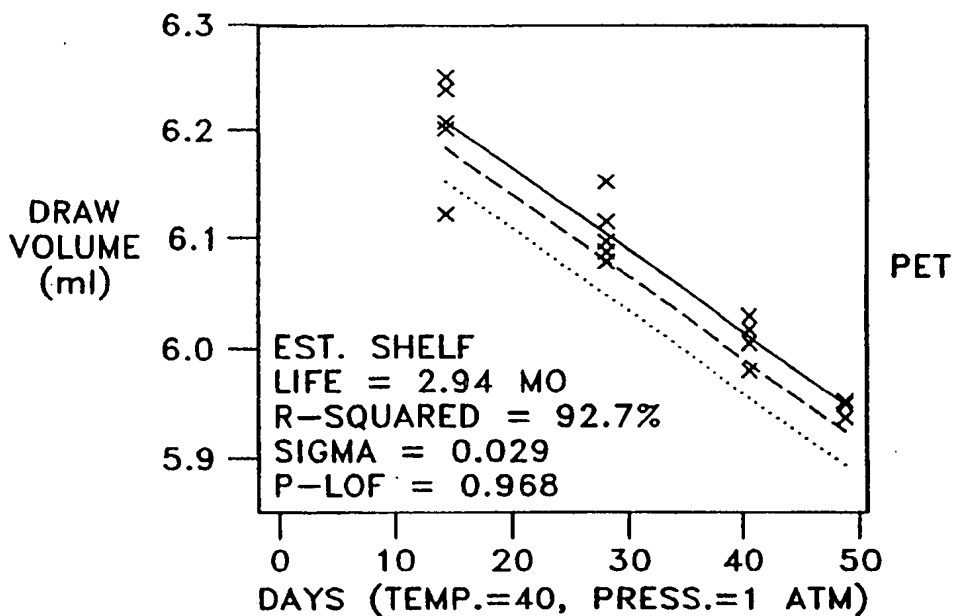
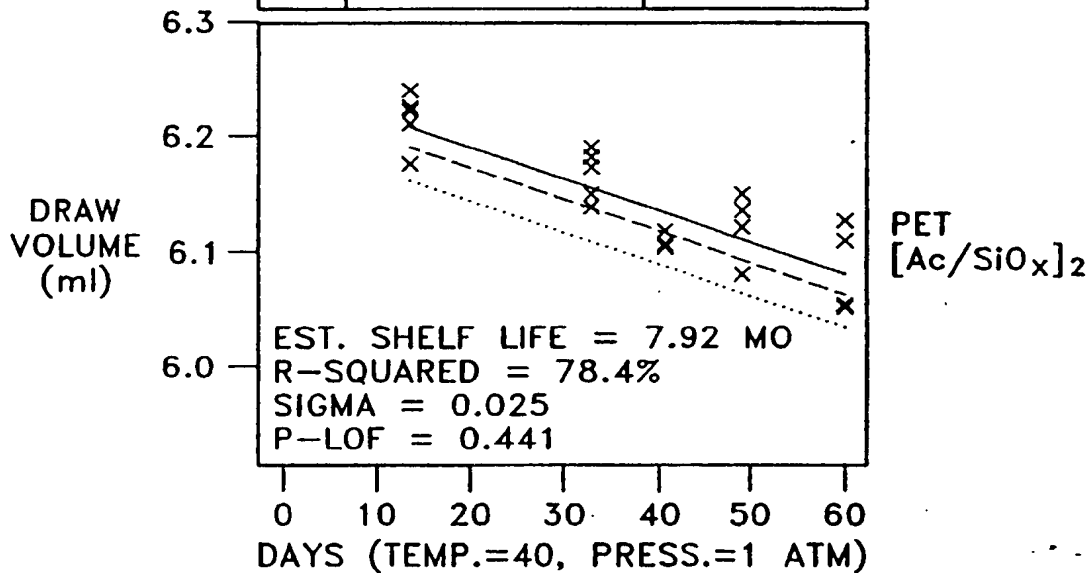


FIG-1

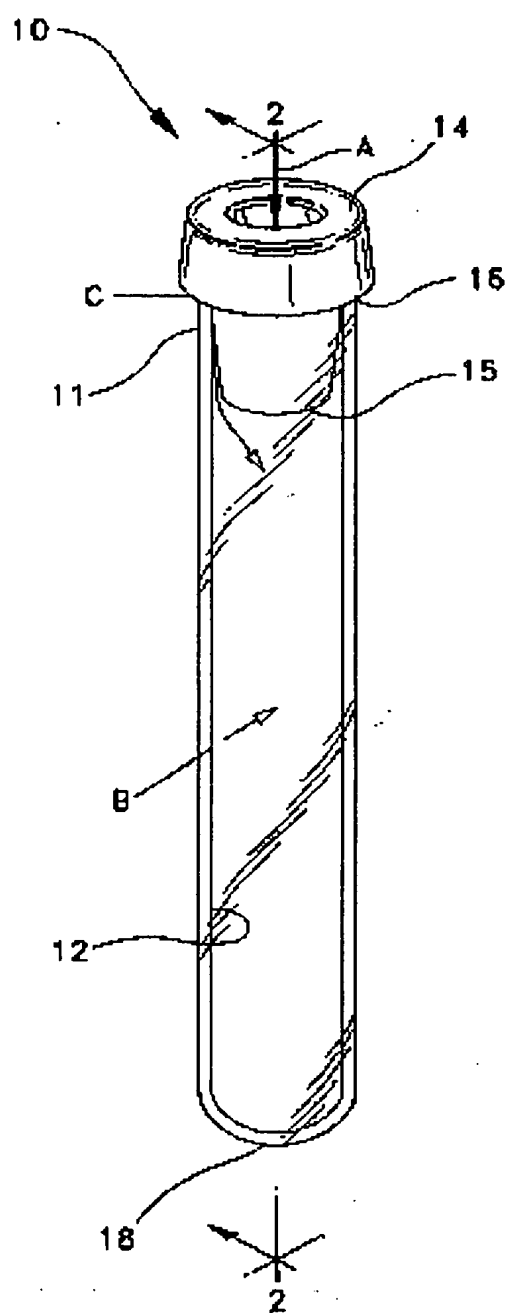


FIG-2

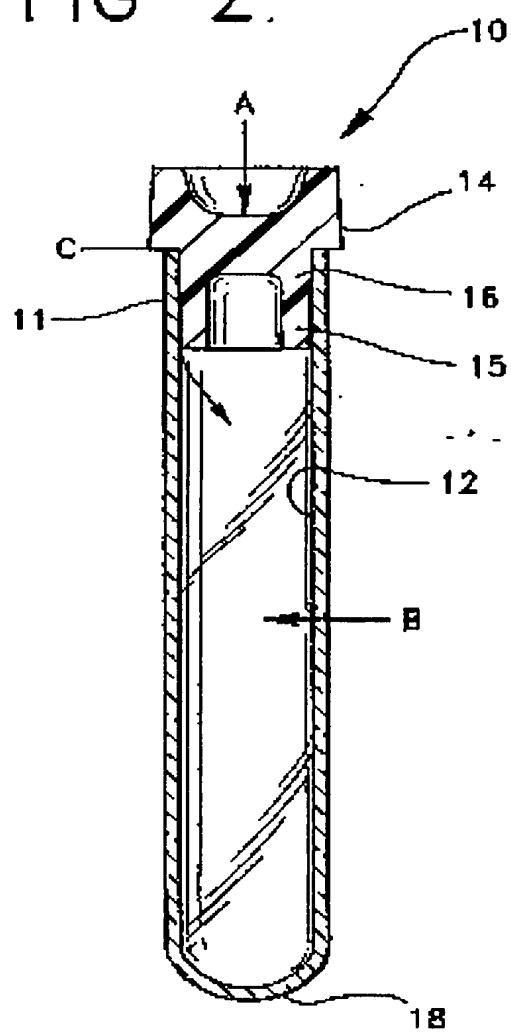


FIG-3

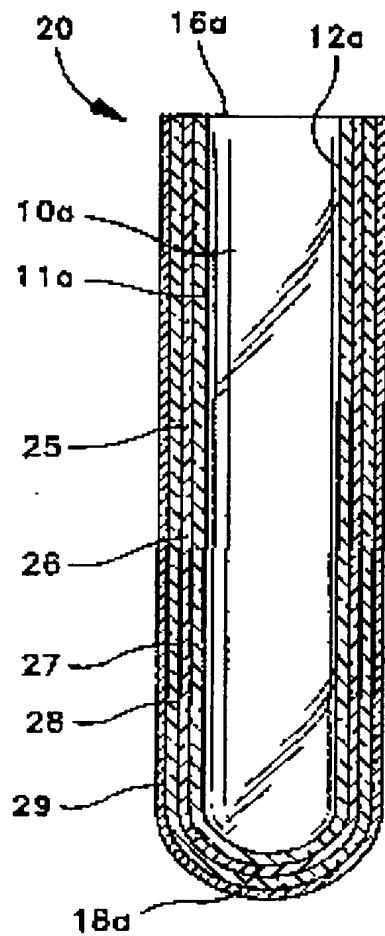


FIG-4

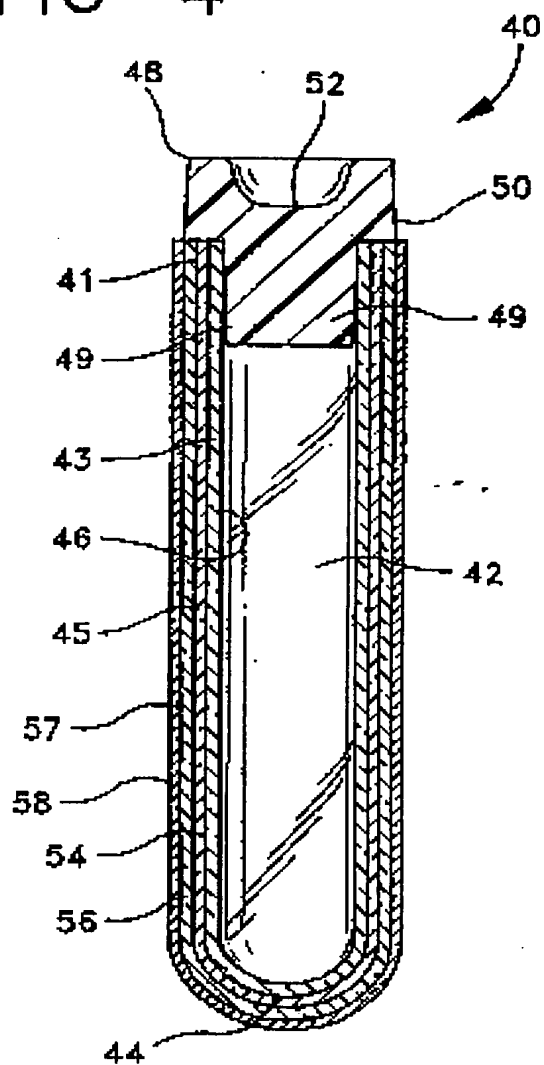


FIG-5

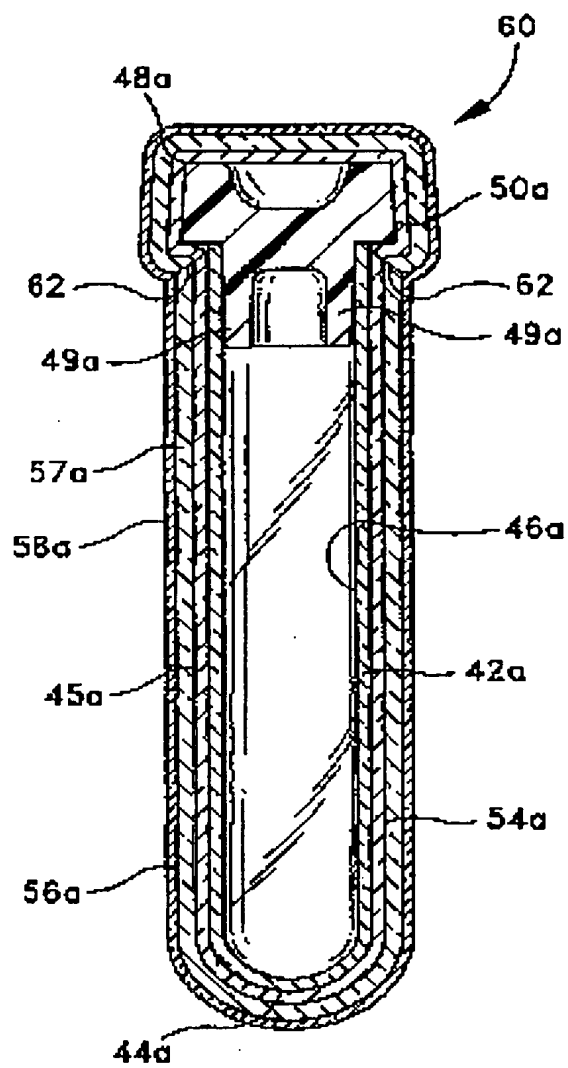


FIG-6

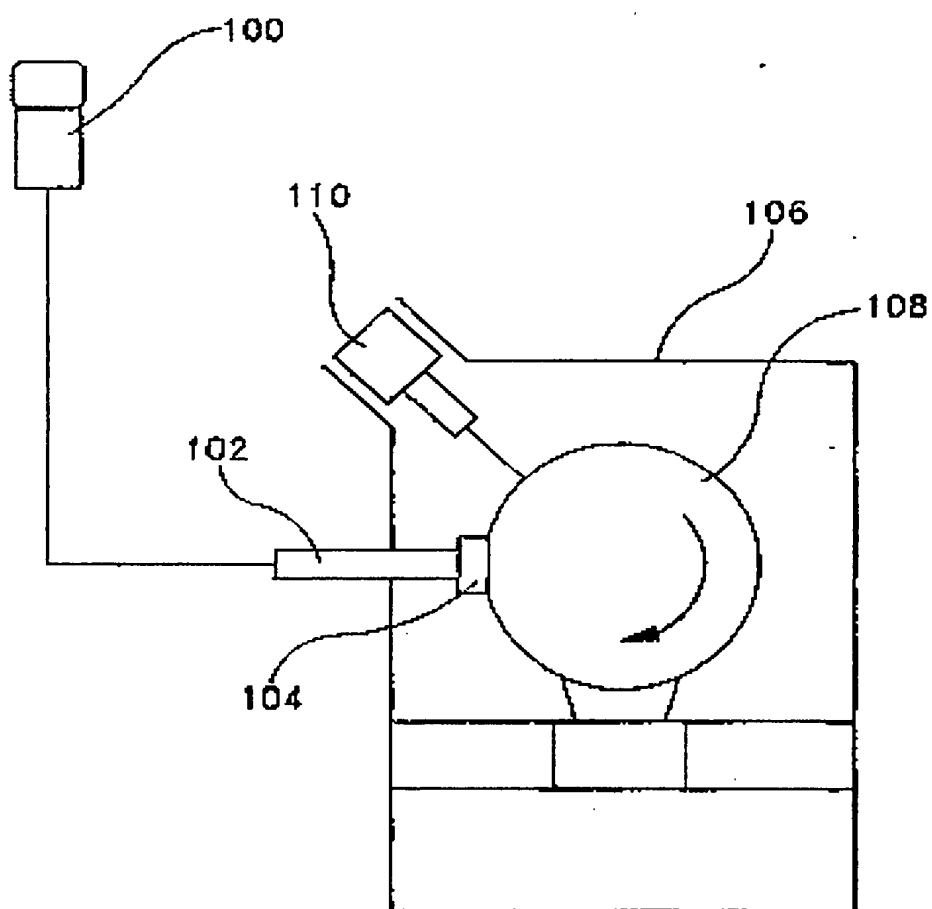


FIG-7

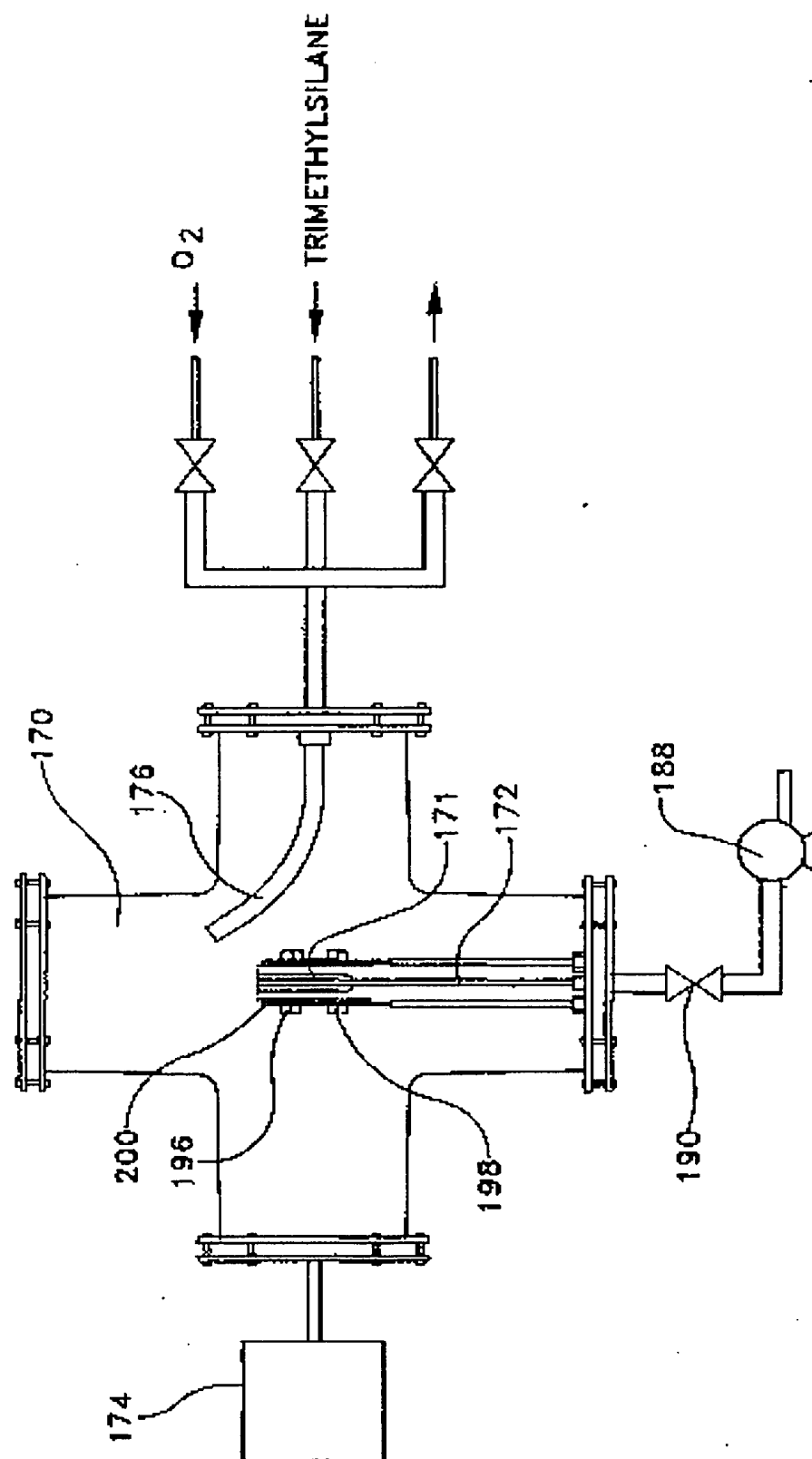


FIG-8 ARRHENIUS PLOT OF OXYGEN TRANSPORT THROUGH PET, PET/SiO_x, AND SiO_x/PET/SiO_x BARRIER FILMS

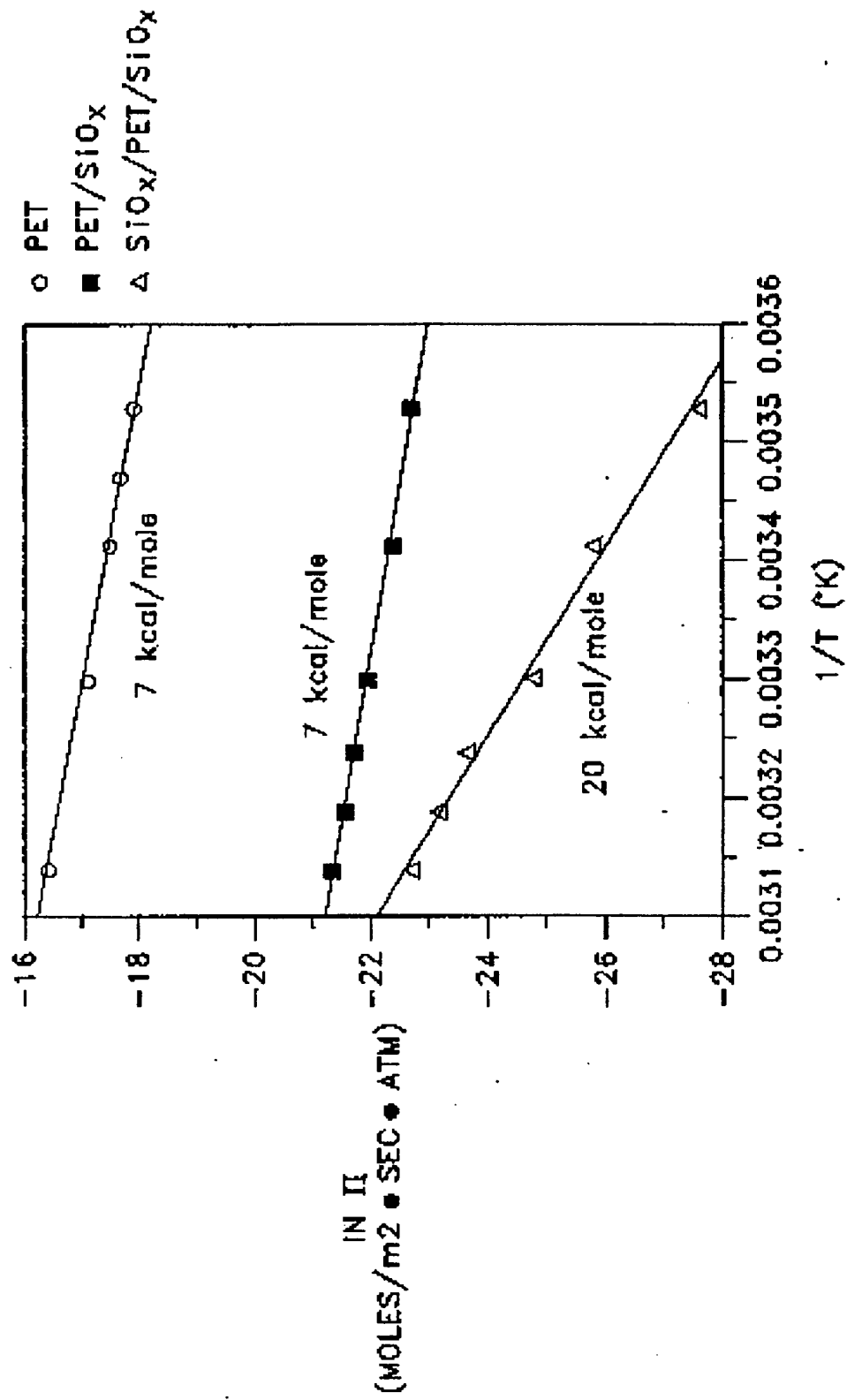
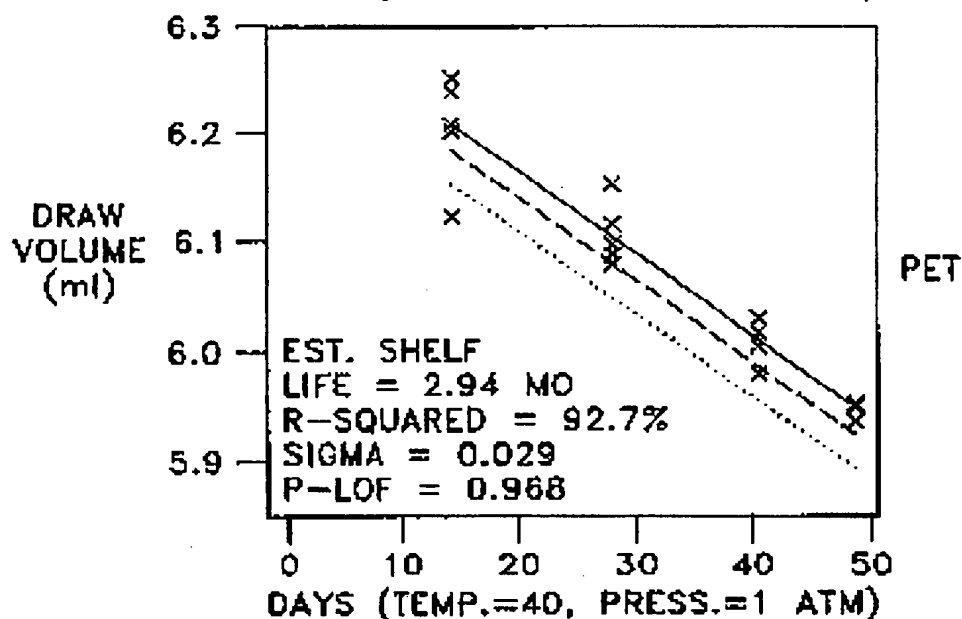
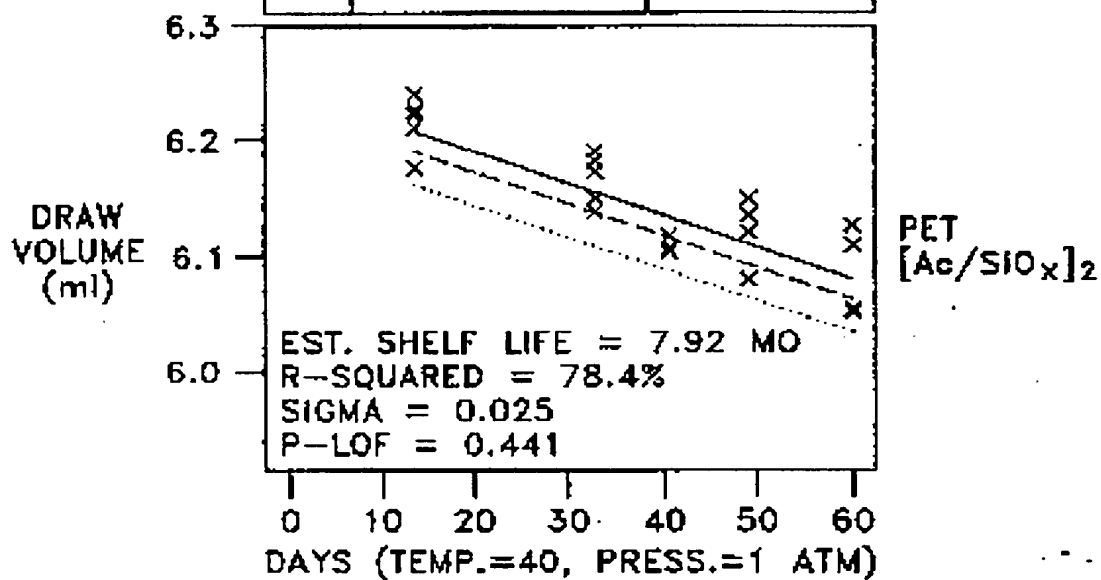


FIG-9 DRAW VOLUME LOSS FOR
 PET/[Ac/SiO_x]_n TUBES AT 40°C, 1 ATM

n	DRAW LOSS (% PER YEAR)	SHELF LIFE (MONTHS)
0	41	2.9
1	41	2.9
2	17	7.9
4	12	13.7





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B05D 7/00

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(54) **Non-Ideal Barrier coating sequence composition**

(57) The present invention is a non-ideal barrier coating sequence composition comprising oxides and organic polymers. The non-ideal barrier coating sequence composition is useful for providing an effective barrier against gas permeability in containers and for extending shelf-life of containers, especially plastic evacuated blood collection devices.

Description**BACKGROUND OF THE INVENTION****1. Field of the Invention**

This invention relates to a non-ideal barrier coating sequence composition for providing an effective barrier against gas and water permeability for containers, especially plastic blood collection tubes. In particular, the barrier coating composition of the present invention comprises the combination of thin films of inorganic oxides and organic polymers, such as highly crosslinked organic thermoset plastics. The composition of the present invention has improved barrier to oxygen and water vapor transport than would have been predicted from the barrier characteristics of either the individual oxide and organic polymer films.

2. Description of the Related Art

With the increased emphasis on the use of plastic medical products, a special need exists for improving the barrier properties of articles made of polymers.

Such medical products that would derive a considerable benefit from improving their barrier properties include, but are not limited to, collection tubes and particularly those used for blood collection.

Blood collection tubes require certain performance standards to be acceptable for use in medical applications. Such performance standards include the ability to maintain greater than about 90% original draw volume over a one year period, to be radiation sterilizable and to be non-interfering in tests and analysis.

Therefore, a need exists to improve the barrier properties of articles made of polymers and in particular plastic evacuated blood collection tubes wherein certain performance standards would be met and the article would be effective and usable in medical applications.

Glass-like or metal oxide films synthesized from chemical vapor deposition techniques have been used as thin barrier coatings on polypropylene films. However, glass-like thin films that are synthesized are substantially granular in morphology instead of substantially continuously glass-like and therefore do not have the oxygen and water vapor barrier characteristics of a truly continuous glass-material.

It has been shown that to overcome the drawbacks of the morphology of glass-like thin films is to "stack" layers of glass-like films with a continuous organic polymer film interposed between each layer. Such laminar multilayer coatings improve the oxygen barrier performance of polypropylene films, however such layering does not produce a glass-like barrier and the layering merely performs as a laminate of metal oxides and acrylate polymer coatings.

It is therefore desirable to produce a composite that may be used to achieve gas and water barrier performance similar to glass.

SUMMARY OF THE INVENTION

The present invention is a plastic composite container comprising a non-ideal barrier coating sequence composition. The non-ideal barrier coating sequence composition desirably comprises organic and inorganic materials disposed over the outer and/or inner surface of the previously formed composite container whereby the barrier performance of the barrier coating composition as a whole is greater than the lamination of each individual material in the whole composition.

Preferably, the non-ideal barrier coating sequence composition comprises a sequence of materials comprising organic and inorganic materials applied to the outer surface of the previously formed composite container.

Most preferably, the sequence of the materials may be expressed as follows:

$$\text{Sequence} = \sum_n (\text{organic material} + \text{inorganic material})$$

where $n = 1-20$

Desirably, an organic material is preferably a highly cross linked acrylate or acrylic polymer.

Preferably, the organic material is a blend of monoacrylate (i.e., isobornyl acrylate) and diacrylate monomers (i.e., an epoxy diacrylate or a urethane diacrylate) as described in U.S. Patent Nos. 4,490,774, 4,696,719, 4,647,818, 4,842,893, 4,954,371 and 5,032,461, the disclosures of which are herein incorporated by reference. The organic material is cured by an electron beam or by a source of ultraviolet radiation.

Most preferably, the organic material is formed of a substantially cross linked component selected from the group consisting of polyacrylates and mixtures of polyacrylates and monoacrylates having an average molecular weight of

**ANNEX TO THE EUROPEAN SEARCH REPORT
ON EUROPEAN PATENT APPLICATION NO.**

EP 97 10 1065

This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report. The members are as contained in the European Patent Office EDP file on
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23-03-2001

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